ADSORPTION CAPACITY OF EUCALYPTUS WOOD CHARCOAL

THESIS SUBMITTED TO

THE BUNDELKHAND UNIVERSITY, JHANSI

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

2002

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KAVITA PUROHIT

UNDER THE GUIDANCE AND SUPERVISION OF

DR. P.C.SINGHAL

READER IN CHEMISTRY

BIPIN BEHARI COLLEGE, JHANSI

INDIA

Dedicated to my father-in-law ***(Late) Shri. Shyam Behari Sudehely****, whose inspiration, love and support to achieve highest echelons has led me to the fulfillment of this work.*

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Dr. P.C.Singhal
M.Sc., Ph.D.
Reader in Chemistry
Bipin Behari P.G. College,
Jhansi.

Res: Shaktinagar
Gwalior Road
Jhansi.
Pin: 284 001 (U.P.)

CERTIFICATE

This is to certify that the research work entitled "***Adsorption capacity of Eucalyptus wood charcoal***" being submitted by Mrs Kavita Purohit for the award of Ph.D degree in Chemistry, contains original piece of research work. It is further certified that the thesis embodies the work of candidate herself.

The candidate had worked under my guidance and supervision for the period required under the University's Research Ordinance-7. The candidate has put the required attendance in the department during this period.

Date: 23rd December 2002.

(Dr. P.C.Singhal)

Acknowledgements

My acknowledgements shall be forever to the capable guidance of my supervisor Dr. P.C. Singhal, Deptt. of Chemistry for granting me an opportunity to work under him. His interest, criticism, meticulous planning, enduring patience, endless support, and advice have led to the timely and successful completion of the work.

It is my privilege to express my sincere gratitude to Dr.U.P. Singh, Principal B.B.C. Jhansi for extending all possible help and support, necessary for this work. I am grateful to Dr.K.C.Kanchan for the generosity to provide laboratory facilities, Dr.A.K.Srivastava, Dr.J.P.Tripathi, and Dr.V.I.Sharma for the appreciation and encouragement during the long and difficult span of this work.

I am highly acknowledged to the authorities of archives of Central library, BHU Varanasi, Indian Agricultural Research Institute (IARI) New-Delhi, Central Library Delhi University, New-Delhi for granting me permission for consultation and allowing reprographs of priceless articles and papers.

I wish to thank Dr.Nita Shandilya whose encouragement and valuable suggestion has helped me to keep the pace of work throughout. My present acknowledgements can never be complete without expressing my gratitude to Mr. Ambarish Shandilya who allowed me access to railway workshop.

present acknowledgements can never be complete without expressing my gratitude to Mr. Ambrish Shandilya who allowed me the facility to work in railway workshop.

I wish to offer my sincere gratitude and regards to my father and mother whose blessings have helped me to successfully end this onerous task. I am thankful to my brothers Ashish, Amit, Navneet and sister Vineeta and my bhabhi's Neetu and Anshu for their invariable help and moral support during the progress of this work.

I am grateful to my mother-in-law for her blessings and support and my inexpressible thanks to my brother-in-law Bobby, Rinku and sister-in-law Jyoti for their co-operation and who cheerfully took day-to-day pains during the various stages of my work.

No words are sufficient to express my acknowledgements for the unflinching support of my husband, Mr Ravindra Sudehely, and who took endless pains in accompanying me to various archives outside Jhansi.

Last, but not the least, I wish to acknowledge, especially Hirdesh, Shantanu, and all those who had contributed to me generously all help, support and assistance to make this work a success.

Kavita Purohit

Kavita Purohit

introduction

INTRODUCTION

In recent years rapid increase of population, urbanization, industrialization, green revolution in agriculture, and various other developmental activities have deteriorated the nature due to addition of different kinds of undesirable substances in the environment.

It is found that continuous disposal of untreated wastewater from various industries e.g. textile, dyeing, leather, carpet, chemical (dye and paint), pulp & paper, sugar, etc., is continuously deteriorating the quality of water due to addition of toxic as well as coloured effluents from various industries using different dyes and metals. These untreated effluents are highly toxic as they contain large number of metal complexes and dyes, which is highly deleterious to all living beings. The industries discharge untreated water on land and in natural streams, the textile industries being one of them.

The wastewater of varying colour comes out of the textile industries. Many people, who perform the dyeing works at small and large scale manually,

allow the drains to directly discharge in the rivers, lakes, and ponds, etc. This untreated coloured water mainly consists of different kinds of dyes. These dyes are toxic to organisms and may result in total destruction of aquatic communities. The coloured wastewater of textile and other industries is leading to reduced penetration of light, which hinders the photosynthesis process in aquatic media, resulting in the reduction of dissolved oxygen (D.O.) and increase in the Biochemical Oxygen Demand (B.O.D.) of the water. These are displeasing on aesthetic ground.

Similarly, the presence of certain heavy metals (e.g. Cr, Cu, Co, Hg) in wastewater, used as mordant in dyeing processes, is affecting the health of all living beings. Not only this, the high concentration of the metals in wastewater destroys the soil fertility and ultimately affects plant growth and consequently agro-based industries. Further, the high concentration of such dyes may cause water-borne diseases such as typhoid, cholera, jaundice, diarrhoea, dysentery, paratyphoid fever, bone marrow injury, etc.

Untreated industrial wastes discharged into lakes and streams are resulting in serious problems of water pollution. Some unwanted dissolved mineral cause hard water problems for industrial and municipal water supplies. Biological activity of the streams may be altered by the discharge of toxic chemicals, which is increasing the acidity and alkalinity on reaction with water to the extent of making it corrosive. Chemicals that need more oxygen gives rise to the problem of de-oxygenation, changing the biological pattern, and thus adversely affecting the entire living organisms.

Water purification represents the main, well-established, and refined technology. Possibly, the most recent technology that has and will contribute in future to alleviating water pollution is that of water re-use, recycling, and in-plant treatment of water for manufacturing and processing purposes.

So, the solution lies in the immediate necessity to remove the dyes/colours from wastewater and making the precious water reusable. This will not only control water pollution but will also avert the future water crisis and thus, will save the entire

aquatic and human community. Hence, it is increasingly important to treat polluted water by physico-chemical processes.

Various methods have been used in the past for purification of water and wastewater containing organic and inorganic pollutants. These processes are based on the principles of precipitation, coagulation, ion exchange, sedimentation, filtration, chemical oxidation, etc.

The adsorption process has been found to be quite attractive especially for the removal of organic pollutants and decolourisation of water and wastewater. Adsorption process is preferred due to its low cost, simple design, easy handling, and sludge free operation.

ADSORPTION

Surface of a liquid is in a state of strain or unsaturation due to the residual or unbalanced force, which act along the surface of the liquid. Similar to this, the surface of a solid may also have residual forces or valencies. Thus, the surface of a solid has a tendency to attract and to retain the other species

(gas or liquid) with which such surface comes in contact.

When a solid surface is exposed to gas or liquid, molecules from the gas or liquid concentrate at the surface of the solid.

"This phenomenon of concentration of molecules of gas or liquid at the surface of solid is called Adsorption".

OR

"Accumulation or retention of atoms, molecules or ions at the surface or interface between any two phase like gas-liquid, gas-solid, liquid-liquid or liquid-solid is known as Adsorption".

The solid that is used to adsorb gases or dissolved substances is called adsorbent and the adsorbed substance usually is referred to as adsorbate.

OR

The material on the surface of which adsorption takes place is called adsorbent and the substance adsorbed is called adsorbate.

When solid substance is dissolved in liquid to form solution, the solute usually tends to concentrate either on the surface or in the bulk of the solvent e.g. soap solution (positive adsorption). On the other hand, the table salt tends to concentrate in the bulk of the aqueous solution rather than on its surface (negative adsorption).

The outside materials penetrating the bulk of the substance leads to the phenomenon of Absorption. In absorption the substance is distributed throughout the body of the solid or liquid to form a compound or solution respectively. Thus, the adsorption is a surface phenomenon and absorption is a bulk phenomenon. As the distinction between adsorption and absorption is not very sharply defined, Mcbain (1909) introduced the general term SORPTION that includes both the adsorption and absorption.

There are essentially three consecutive stages associated with the adsorption of materials from solution by porous adsorbents. They are:

1. The transport of the adsorbate to the exterior surface of the adsorbent.

2. The diffusion of the adsorbate into the pores of the adsorbents. and
3. The adsorption of solute on the interior surface of the adsorbent.

Types of Adsorption: -

The adsorption may be classified into two types depending upon the nature of forces operating between the adsorbate and adsorbent.

1. Physical adsorption
2. Chemical adsorption

1. **Physical Adsorption**

Such type of adsorption is due to the week Vander-Waals forces acting between adsorbent and adsorbate species. It is also referred to as Vander-Waals adsorption. In such cases, the adsorbed molecule is not bounded to a specific site at the surface but, is, rather free to undergo transitional movement within the interface. In this type, the adsorption is favoured at low temperatures and the heat of adsorption is of the order of 5kcal/mole. It is a reversible process.

2. Chemical Adsorption:

In chemical adsorption, strong attractive forces are operative in the formation of new bonds between the adsorbate species and active centres of the adsorbents. Chemical reaction at a surface may either be exothermic or endothermic, and an increase in temperature will decrease or increase the amount of product formed. The heat of adsorption lies in the order of 20-100kcal/mole. It is an irreversible reaction.

Factor Influencing Adsorption:

Various parameters, which affect the degree of adsorption, are given below: -

1. Nature of adsorbent
2. Nature of adsorbate
3. Nature of solvent
4. Temperature
5. pH
6. Concentration

1. Nature of Adsorbent:

The adsorption process is largely dependent on the physico-chemical properties of the adsorbent such as surface area, particle size, porosity, and

residual charges on the surface of the adsorbent. The pre-treatment of the surface of the adsorbent by heating, grinding and cleaning is also responsible for affecting the adsorption.

2. **Nature of Adsorbate:**

The adsorption at a solid surface takes place by the attraction of the adsorbate molecule due to its residual forces. The adsorption of a solid-solution interface is greatly influenced by the physico-chemical characteristics of the adsorbate like weight, molecular size, electrical charge, the degree of dissociation, solubilization, and ionization.

3. **Nature of Solvent:**

The polarity and dielectric constant of the solvent affect the adsorption process to a great extent. The effect of solvent on adsorption has been studied by Freundlich and Heller[1]. They observed that the addition of non-aqueous solvent to an aqueous solution increase the adsorption of Sr (II) and other cations on different oxides.

4. **Temperature:**

Adsorption process is greatly affected by temperature. The rate of adsorption generally increases with decreasing temperature, but in few cases the rise in temperature favours the rate of adsorption[2].

5. **pH**

The pH of adsorbent-adsorbate system affects the rate, extent and mechanism of adsorption. On increasing the pH of the solution, adsorption of cations increases[3] and that of anions decreases[4].

6. **Concentration:**

The ionic concentration of an electrolyte solution has remarkable effect on the uptake of the ions by the surface of adsorbent. It is found that the process of adsorption at any particular temperature becomes more complicated due to the formation of mono and multilayer adsorption as well as capillary condensation Giles and coworker[5] have reported various types of adsorption isotherms. Adsorption of some ions obeys Langmuir adsorption isotherm,

$$qe = Q^0bc/(1+bc) \quad \text{where,}$$

qe = amount of adsorbed dye per gm of adsorbent.

c = is the equilibrium concentration

Q^0 and b are Langmuir constants.

Freundlich also gave an equation applicable within limited concentration range:

$$qe = K_f\, c^{1/n}$$

K_f and 1/n are Freundlich constants. However, at low temperature and micro concentration i.e., when 1/n becomes equal to unity the equation obeys Henry's Law:

Henry's Law :

$$qe = kc$$

If, Langmuir or Freundlich isotherm fails to explain the adsorption data, Sips adsorption isotherm given below has been found quite useful:

$$qe = Q^0 c^{1/n}/(b+c)^{1/n}$$

The phenomenon of adsorption finds extensive application in various fields. Applications of adsorption includes: animal charcoal for removing of colour in manufacture of cane sugar and is also

used for the removal of odour from refrigerator and in general air conditioning procedures. The gels are used in air conditioning systems for deodorization[6], which are made of synthetic fiber tied with transition metal chelate catalysts. Also nets with activated carbon and apatite are used as disinfectants.

Activated charcoal is used in the preparation of gas masks. Charcoal adsorbs all toxic gases and vapours from air and allowed only pure air to pass through the pores of it. Anand Shrinivasan[7] et al have used zeolite, made by fly ash for the adsorption of SO_2. It is also used in removing hydrocarbons from natural gas, oxygen, nitrogen or other gaseous impurities from helium during the separation and purification of later. The paper used in cigarettes is prepared from coconut shell that behaves as activated charcoal (adsorbent) and hence removes harmful substance liberated during smoke[8].

Colloidal silica and aluminum gels are used for removing moisture and for controlling the humidity of rooms. Colloidal silica is used to remove or adsorb impurities from petroleum oil, motor spirits, and waxes.

Adsorption from solution has found more applications than that of gas phase. Adsorption has been used in dyeing, photography, brewing, and purification of water, clarification of oil and in making various lubricants. It is also used in chromatography, titration (as indicator), for softening and de-ionization of water.

The phenomenon of adsorption plays an important role in the heterogeneous catalysis e.g. finely divided iron and nickel is used in Haber's process for the manufacture of ammonia and hydrogenation of oil respectively. Liquid phase adsorption has been shown to be effective for removing suspended solids, odours, organic matter and oil from aqueous streams.

Adsorption process is useful in the extraction and purification of gold and silver[9]. Activated wood char is also useful in extraction and purification of some non-ferrous metals like platinum, palladium and osmium from their dilute chloride solutions[9], pure tungsten oxide from low-

grade ore[10], vanadium from mining waste[9] and rhenium, molybdenum from their leached solutions[9].

Adsorption process is used to remove impurities from liquids. Applications of adsorption have been very important in many fields, such as in purification processes, wastewater treatment, and analytical processes[11].

Activated wood char has been used in medical applications. It is an important material in the manufacture of several types of ayurvedic, homeopathic and allopathic medicines[12]. It is also used in the manufacture of a universal antidote [13]. It is also used in removal of colouring substance (dyestuff) from various type of sugar syrup and purification of many chemical, pharmaceutical, and foodstuff products.

This process of adsorption by activated carbon has come up with extensive usage in wastewater treatment and for removal of unwanted organic materials from various solutions because of its ease, efficiency and economics.

Workers[14] have used different types of adsorbents for the removal of undesirable colour and waste. Alumina[15], calcium carbonate[16], Fuller's earth[17], clay[18] used as adsorbents. Inorganic solid adsorbents like manganese oxide[19], sodium titanate[20], zirconium oxide[21] have been reported as good adsorbents.

Nigerian-sub-bituminous coal palm, kernel shell, and cow-bone have been found to be good adsorbents[22]. Several waste materials like unio and pila[23], buffing dust[24] have been also used in adsorption process. Certain low cost materials like coal[25], peat[26], sawdust[27], and spent bleaching earth[28] have been reported as efficient adsorbents for the decolourisation and removal of waste.

Owing to the high cost of activated carbon, many researchers have used agricultural waste material as adsorbents, due to its low cost and easy availability. They have used rice husk[29], soya bean hulls and cotton-seeds[30], seed shell powder[31] as efficient adsorbents.

The total earth consists of 70% water and the remaining 30% consists of land and green cover consisting in-numerable varieties and species of flora and fauna. Since time-immemorial man has been dependant on this green cover for one or the other purpose ranging from food, clothing and shelter.

They have been of great interest and importance due to different useful materials derived from them like fruit, leaves gum, tannin, rubber, nuts, wood, oil, bark which are useful in different preparations like medicines, oils and various other extracts. They are useful as they participate in photosynthesis process converting CO_2 (one of the green house gases, commonly called as GHG's) from the atmosphere into O_2 essential for the survival of the entire animal kingdom.

Fossil fuel is the driving force behind every nations GDP. It is used in ship-building, construction, furniture industries, etc., In terms of value, the most important use of wood is in paper and pulp industry.

Eucalyptus is an exotic plant found all around. It is long and grayish in colour. Its botanical name is ***eucalyptus globulus*** . In India, it is called blue gum tree. It is native of Australia and is cultivated and mainly found in the regions of Nilgiris, Palni hills, Shimla hills, and Shillong and its adjoining region in Assam.

Eucalyptus plant is useful for the treatment of human being in different ways. Eucalyptus oil is very useful and has immense medicinal values and is useful in various other ailments. Eucalyptus oil is obtained by the distillation of dried leaves and terminal leaf-lets. This oil is used in the treatment of asthma and bronchitis and is also used in the perfumery industry. It is largely used as mosquito and as vermin repellent and as an important ingredient for germicidal and disinfectant preparation. It is a vital for de-odorizing and repellent composition for use in theatres. It is also used in manufacture of toothpaste.

In India, eucalyptus appears to be the most important wood species for the charcoal making and as an alternative energy source for iron-making[32].

The principal chemical constituents of wood are cellulose, lignin, resins, and waxes. Among these cellulose and lignin are the major chemical constituents. Their average ultimate analysis and probable empirical formulae are given in the table[33] (1).

Table (1) Average ultimate analysis and probable empirical formulae of the principle chemical constituents of wood:

Const-ituents present	% age of tissue	Average ultimate analysis (%)					Typical formula
		C	H	O	N	S	
Cellulose	45-65	44.4	6.2	44.4			$(C_6H_{10}O_5)_n$
Lignin	20-40	63.2	6.1	30.7			$C_{30}H_{33}O_{11}$
Resins	0.5-15	80.0	10.0	10.0			$C_{20}H_{30}O_2$
Waxes	0.2-14	82.0	14.2	3.8			$C_{29}H_{60}O$

Cellulose is a common constituent of the plant, represented by the formula $(C_6H_{10}O_5)_n$, where the value of n is not known. Lignin is a hard and amorphous substance of intermediate molecular weight. The cell walls of woody parts of plant are strengthened by lignin i.e., it contributes to the

rigidity and support of the plant body. It also affects the yields and properties of wood char produced.

Yatim and Hoi[34] reported the comparatively higher presence of lignin content of 27.9 % in eucalyptus wood. This is due to the presence of comparatively higher carbon content of eucalyptus wood. Kumar et al[35] determined the chemical and physical properties of eucalyptus wood, which are shown in table (2).

Table (2) Chemical and physical properties of eucalyptus wood

Proximate analysis (wt % dry basis)			Ultimate analysis (wt % dry basis)					CV	ASG	TSG	Porosity (%)
VM	Ash	FC	C	H	N	S	O				
82.44	1.17	16.39	57.2	5.25	Nil	Nil	36.38	20.3	0.681	1.510	55.0

where ,

VM : volatile matter

FC : fixed carbon

CV : calorific value, mJ/kg, dry basis

ASG : apparent specific gravity, dry basis

TSG : true specific gravity, dry basis, and
C,H,N,S,O : stands for carbon, hydrogen, nitrogen, sulphur and oxygen respectively

They have analyzed the ash of eucalyptus wood given in table (3).

Table (3) Wood ash analysis

Sample	Composition of Ash (wt %)					
	Na	K	Mg	Ca	Zn	Fe
Eucalyptus wood ash	0.342	25	0.762	8.92	0.0113	0.722

DeGroot and Shafizadeh[36] suggested the comparatively higher carbon content in eucalyptus due to higher lignin content in eucalyptus wood and greater thermal stability of this component.

Wood consists of a network of fibrous cells. The major function of fibers in the woody plant is to give it mechanical support and save the plant from various stresses and strains of environmental forces. The hardwood is generally strong, dense, and heavy due to high proportion of fibers. In eucalyptus[37] wood, dense fibrous cells of cellulose are present making it

hard and strong and useful for char making. Production of pyrolytic carbon at lower decomposition temperature (400°C) is of economic interest and thus eucalyptus wood's volatile matter (VM) in place of hydrocarbon (methane, propane, propylene, etc.,) may be a good source of pyrolytic carbon in future.

With all these properties, it is pertinent for me to say that eucalyptus wood presents a revolutionary characteristics not only chemically due to high calorific value (CV), greater thermal stability, etc., but also biologically because of its fast growing feature and high bio-mass yielding capacity, and its availability in abundance, it was suggested to explore its scope as adsorbents in the present study.

review of literature

REVIEW OF LITERATURE

Adsorption technology is currently being used extensively for the removal of organic and inorganic micro pollutants from aqueous phase since it was first introduced in 1940's. One of the most common uses of the adsorption is for purification of gases and liquids. Its application is to remove moisture, colour, odour, taste, and in general, undesirable components of the mixture without appreciably affecting the desired component. Adsorption is used not only for removal of molecularly dispersed substance from solution, but is also used for removing colloidally dispersed substances[38].

The term carbon is widely used in industry to refer to activated charcoal, which may contain considerable ash. The residue shows little or no decolourising power. Ogawa[39] determined the elementary composition of a sugar charcoal. Bartell and Lloyd[40] have prepared a charcoal by activating purified sugar charcoal in highly oxidizing atmosphere below 150^0C, which approached the

behavior of hydrophilic silica in its adsorptive properties, it gave only negatively charged particles when suspended in water. High temperature charcoal activated near 1000^0C behaved as an organophilic adsorbent and on suspension in water showed both positively and negatively charged particle.

Activated carbon is widely used in wastewater treatment in removing organic and inorganic pollutants in removing coloured impurities from aqueous solution. Possessing high surface area, activated carbon frequently exhibits high removal efficiency for most dissolved compounds[41]. The removal efficiency is influenced by the characteristics of the activated carbon such as surface properties, pore size and chemical chracteristics. In general, characteristics of activated carbon are controlled by the manufacturing process, the nature of raw materials, the nature of activating agents, and the condition of activation process. Perish[42] and Prich[43] recommended the use of activated carbon as it can be regenerated more than ten times.Thus, activated

carbon is a best adsorbent because of its large surface area, high purity, and easy availability.

Activated charcoal is used as an efficient adsorbent for gases, vapours and dissolved substances in electrolytic solutions have an ion exchange properties determinded mainly by the chemical nature of their surface[44, 45]. Bartell and Miller[46] found that pure charcoal activated at high temperature (900-1000^{0}C) in air absorbs anion from electrolytic solution and replace them by an equivalent amount of hydroxy ions i.e., it behaves as an anion exchange in the OH form. A modification of activated charcoal by oxidation in air was first discovered by Dubinin[47] and by Kruyt and Dekadt[48]. It was later shown that carbon sorbent with cation exchange properties could also be obtained by processing activated charcoal by other oxidants in the gaseous [49,50] or liquid phase[51, 52]. The production of activated carbon from by-products and waste materials is reported to have increased[53]. Low temperature (850-900°C) activated carbon can obtained by applying CO_2 stream[54].

The gasification kinetics of carbonaceous material has been investigated by several workers[55]. Carbon was only produced from walnut for adsorption study[56] and several fruits, stones and shells have similar composition and mechanical properties[57]. The carbon is also obtained by destructive distillation of wood or other carbonaceous material. It is activated by heating to 800-900^{0}C with steam or CO_2, which results in porous internal structure[58].

The bone black or bone char is the carbonaceous residue obtained as a result of destructive distillation of bone char in the absence of air. The principle constitution of bone is tricalcium phosphate. Besides this compound bone contains magnesium phosphate, calcium carbonate, some alkaline salts, fatty and cartilaginous matter intimately associated with the mineral content[59]. Mantell[60] has given an analysis of American bone char. Bone char is used in sugar industry for decolorizing of sugar syrup, which is a step in preparing pure crystal of sugar. Coagulants[61-64] used for the removal of dyes from water are $FeSO_4$, Lime, $MgCO_3$, $Fe_2(SO_4)_3$ and $FeCl_3$ by chemical

oxidation using O_3 and Chlorine. Percentage removal of dyes by coagulation method is only partial (60-80%) while adsorption technique is an ultimatum for the removal of dyes from wastewater.

Activated carbon is used for the removal of different dyes from aqueous solution of wastewater. Some investigators have reported the use of activated carbon for the removal of Barium[65], Fluorides[66], methyl mercuric chloride[67], aromatic hydrocarbons[68] and phenyl amide pesticides[69]. Activated carbon has been used by Huang and coworkers for the treatment of wastewater enriched in cadmium [70,71], chromium[72, 73], Mckay[74] used the activated carbon in the adsorption of Victoria blue. The effect of contact time, particle size, initial dye concentration, and agitation rate was studied. It has been used for the removal of Disperse blue-7 from aqueous solution [75]. Mckay[76,77] carried out the batch and column studies on the adsorption of Telon blue, Chlorantine fast orange, victoria blue, Cibacet Turquoise blue and Deorlene yellow on activated carbon from their aqueous solutions. He proposed the B.D.S.T. (Bed Depth Service Time) model.

Kobayashi and coworkers[78] studied the arsenic removal by adsorption on activated carbon.

Huang et al have used activated carbon for the adsorption of cobalt[79], mercury[80], Kulkarni[81] et al used the activated carbon for the removal of Astrazone blue and suggested a complex formation mechanism at the solid-solution interface for metals, organic pollutants, odour control and dyes. Activated carbon was an efficient adsorbent for the adsorption of Omega chrome red ME from its aqueous[82]. Bushra et al[83] gives a solid phase diffusion model for adsorption of basic dyes on activated carbon. Roberto leyva-Ramson[84] studied the effect of temperature and pH on adsorption of anionic detergent on activated carbon. Powdered Activated Carbon (PAC) has been used for colour removal from wastewater by Ruth Yu-Hi[85] .

Granular Activated carbon (GAC) has long been used as an effective adsorbent for wastewater treatment in textile industry. The production of granular activated carbon (GAC) from surplus, low value agriculture waste serves a double purpose. First, it converts unwanted, surplus agricultural

waste of billions of kilograms produced annually to useful, value-added adsorbent. Second GAC are increasingly used in water treatment for removing organic chemicals and metals of environmental or economic concern.

Mitchell and coworker[86] investigated, that, GAC made from pecan and walnut shell adsorb higher level of benzene, toulene, methanol, acetonitrile, acetone and 1,4 dioxane from aqueous mixture than commercial GAC. Oxidized GAC made from soybean hulls, sugar-cane bagasse, peanut shell and rice straw adsorbs higher amount of Pb(II), Cu(II), Ni(II), Cd(II), and Zn (II) than any commercial GAC.

The GAC made from agricultural by product have considerable potential for adsorption of organics and metal of environmental concern. K.C.Lakshami Rao[87], used four type of GAC for removing different dyes from wastewater, suggested that granular activated carbon was used because GAC can be easily regenerated and re-used. The cycle of regenerated carbon holds the key to the

economic viability of activated carbon adsorption for wastewater.

PAC and GAC have long been used as effective adsorbents for wastewater but they are expensive owing to high cost, tedious procedure for preparation and regeneration of activated carbon. There is a continuous search for low cost, easily available, potential adsorbent for wastewater. Many researchers have focused these investigations on relatively cheaper and commercially available waste material such as maize cob, fly ash, carbonaceous wool, clays, benolite, bone char, turkey feather, human hair and agricultural by-products. Several investigators have used low cost waste material as adsorbent.

Silica or silicic acid is inert and a good adsorbent for polar substances. Bartell and Almy[88] have discussed reproducible activation of silica gel. They have suggested that gel should not be heated above 300^0C. With Bartell and Almy's sample of gel, the maximum activity was produced by heating for 2 hrs at 300^0C. Adsorbed water was still present and could be driven off at high temperature, but it

appeared that under these condition the gel structure collapsed.

Several workers[89,90] have reported the separation of phospholipids using silica gel earlier. Silica gel carried out the removal of colours from textile efluents[91]. Alexander and coworkers[92] studied adsorption kinetics and diffusion mass transfer processes during colour removal from effluents. McKay et al[93,94] have used silica for colour removal from textile effluents. They have proposed a three-step model for the adsorption of Astrazone on silica gel. Ram[95] has studied the time rate adsorption of dyes on silica. Silica has been used for adsorption of basic dyes from aqueous solution by McKay[96]. They gave solid diffusion model for adsorption study of basic dyes.

Silica gel has good capacity for the adsorption of cobalt (II) ions from solution containing metal ions and organic ligands[97]. Ram et al[98] performed the kinetics of removal of Basic blue-3 from textile effluent using silica gel as an adsorbent. The adsorption was found to follow a first order kinetics. Parameters investigated are concentration,

temperature, pH of dye solution and presence of electrolytes and surfactants. Bajpai and Dengre[99] gave adsorption of milk protein, casein at silica-solution interface. The adsorption behavior of some styryl pyridinium dyes on alkali treated silica bas been investigated by Sudam and Mishra[100]. The surface area of alkali silica is found to be more than the untreated silica. The adsorption isotherm and adsorption kinetics have been discussed in light of the molecular behavior of the adsorbent. Jong Sung Kim et al[101] investigated selective removal of Cu ions from aqueous solution by modified silica beads impregnated with Lix.

Zeolite, a crystalline hydrated aluminum silicate of alkali metal with three dimensional anion network, has been used as an adsorbent for separation of phospholipids by thin layer chromatography[102]. Banerjee[103] carried out the adsorption and desorption studies of Crystal violet and Malachite green on synthetic zeolite3A and AW500, where Crystal violet was more extensively adsorbed than Malachite green. Zeolite has efficient capacity for the removal of chromium ions from solution[104]. The uses of zeolite for separation of

organic acid, amino acid, carbohydrates[105], textile dyes[106], and food dyes[107] has been reported by several workers. Zeolites have been utilized to remove Pb and Ni ions from wastewater and aqueous solution[108].

The clay minerals comprise a wide variety of substances, which can be used as adsorbents. The minerals are crystalline substances of colloidal dimensions, which show exchange properties to varying degree. The behaviors of clays are related to the size shape and composition of particles present and to their exchange properties[109]. Montmorillonite, kaolinites and some bentonites are composed of platelets. In composition, these substances are silicates, kaolinites and alumino-silicates. The bentonites are also alumino-silicates, but, more complex.

Clay can be used to remove coloured component from oil and bone char and is used to remove impurities from sugar solution in sugar refining[110]. Several workers demonstrated the use of clays for the removal of lead[111, 112]. Clays are known to adsorb basic dyestuff from aqueous

solution. Reciprocal plots are linear, indicating a monolayer adsorption of these dyes[113]. Sethuraman et al[114] has used clay for the removal of colours. They investigated kinetic study of adsorption of cationic and anionic dyes.

Montmorillonite has been used for the removal of cadmium by Garcia and co-worker[115]. Montomorillonite, illite and kaolinite have been utilized to remove pyridine from its aqueous solution[116]. Frost and Griffin[117] carried out the removal of arsenic and selenium by adsorption from municipal landfill lichate on to kaolinite and montmorillonite. Pandey et al[118] used wollastonite for the adsorption of Cr(vi) ions from aqueous solution. The adsorption of cadmium by montmorillonite vermiculite, biotite and kaolinite minerals were reported by Zipper et al[119]. Montmorillonite has been used for the removal of phenol from wastewater and aqueous solution[120]. Singh et at[121] reported 95% removal of Congo Red from wastewater by wollastonite around pH-3.0. The studies show that the adsorbent can be regenerated and dye can be recovered.

Gupta and coworker[122,123] found that wollastonite, a mineral found in plenty in India, can be used as potential adsorbent to treat textile effluent rich in Omega chrome Red ME, Metaomega chrome, Orange GL, and Omega chrome Fast Blue B. Wollastonite has very good capacity for removal of Fe(II) ions from water[124]. Cahit Eylem and coworker[125] have used kaolinite, montmorillonite, and chlorite for the adsorption of barium ions. Mordenite clay used as an efficient adsorbent for the removal of cadmium[126]. Montgomery et al[127] investigated the use of organophilic clays as adsorbents for removal of organic components of industrial waste prior to conventional cement based solidification. These industrial waste containing between 2-12% organic carbon and trace of heavy metal and various other contamination were treated with free quaternary ammonium salt exchanged clay. The organic component of all three wastes was well adsorbed by clay.

Clay minerals are good adsorbents for removal of Zn ions[128]. Treatment of effluents of carpet and metallic industries rich in certain chrome dyes and heavy metals have been carried out by Singh and

coworkers[129] using wollastonite as an adsorbent. The dynamics of adsorbate transport from bulk to solid phase has been studied in light of their adsorption on the outer surface as well as diffusion within the pores of wollastonite. The adsorption data fit to the Langmuir's isotherm model. Natural and activated bentonites have been used for adsorption of Cd, Zn ions from aqueous solution by Gonzaleoz et al[130]. Kaolinite clay has good capacity for adsorption of Pb from water[131].

Fuller's earth and other clays are used in extremely large quantities for bleaching, decolourizing, catalysis, and other applications. Fuller's earth has been reported to have high natural adsorptive power[132]. Large quantities of fuller's earth are used in purifying petroleum products[133]. Mckay et al[17, 134] showed that fuller's earth is more effective than fired clay for the treatment of Astrazore Blue and Telon Blue under various parameters such as agitation rate, initial dye concentration, adsorbent mass and temperature. The kinetics study showed that the rate of adsorption was totally controlled by boundary layer film diffusion. To explain the results, they proposed

a kinetic model. The adsorption of dyestuff, Telon Blue (Acid Blue 25) on Fuller's earth and Astrazone Blue on to fired clay has been studied[135]. Bajpai and Viswekarma[136] have used Fuller's earth for the removal of polyacrylamide. China clay has been used in past for the removal of fluoride[137], Zn[138], Chromium[139] from wastewater.

Sorption of cadmium at low concentrations on two denis soils (Loamy sand and sandy loam) was examined by Christensen[140]. Removal of arsenic(III) and boron by soil may be influenced largely by level of allophanes, amorphous iron oxides and hydroxides[141]. Sorption and desorption of Co was studied on different soils and different components by Bansal[142]. Jona et al[143] investigated sorption of carbofuran (2,3 bihydro 2,2 dimethyl benzo furayl, methyl carbonate) by soil.

Alumina has been used in chromatography. It is a good adsorbent for most substances (with the proper solvent), has large capacity, and is white, insoluble, reasonable, chemically inert, and readily obtainable. Alumina has been used as a mean for removing fluoride from domestic water[15, 144]. The

mechanism of various azo dyes on chromatographic alumina has been studied using spectrophotometric technique[145]. The adsorption characteristics of cationic dyes have been studied over alkaline chromatographic alumina powder[146]. Removals of phosphate ions from domestic wastewater have been tested[147, 148]. Several workers have used alumina for the adsorption of arsenic[149] and lead[150]. Selenium[151] and natural organic matter[152] from potable water has been removed by alumina.

The interaction of dyes with alumina has also been studied[153]. Mundhra et al[154] carried out the adsorption of Orange and Napthol Blue Black on HCl treated alumina.

Sorption and desorption behaviors of three oxyanions (MnO_4-, CrO_4- and VO_3-)on chromatographic alumina prepared with HNO_3 has been described[155]. Adsorption behaviors of some amino acids on chemically prepared alumina has been discussed[156]. Bajpai and Rajpoot proposed to alumina for the adsorption of sulphonilamide from its aqueous solution. The ability of heterogeneous mixture of alumina and clay for the removal of dye

has been tested by Khatri et al[158]. The adsorption of maltose from its aqueous solution performed on to alumina surface[159]. The adsorption at pH 6.0 and temperature 30°C obeys the Langmuir's model.

Bagasse fly ash, a waste generated in sugar industries, has been converted into low cost adsorbent material and can be utilized for the removal of phosphate ions from its aqueous solution[160]. Several workers have investigated fly ash as an effective adsorbent for the removal of colours[161]. Gangoli et al[162] studied the feasibility of chromium(VI) removal by fly ash adsorption. Chromium[163] and copper (II) [164] are successfully removed by fly ash at various parameters. Some investigators[165] used fly ash and ash obtained by incineration of used tea dust or leaves as adsorbents for removal of colours from effluents rich in red dye. Khare and coworkers[166] employed fly ash for the removal of Victoria blue at different pH and concentrations. They observed that with diffusion-controlled nature the process followed first order rate expression at pH 8.0.

Gupta et al[167] carried out the removal of a chrome dye Metamega chrome orange GL from water by fly ash. A 98.45% removal was achieved in 110 minutes of equilibrium at 10mg/l concentration, 30^0C temperature, and pH 3.0. Correlation between intra-particle diffusion rate constant and studied parameters was developed. Some investigators investigated the removal of Ni[168] and fluorides[169] from aqueous solution by fly ash. Workers[170] investigated the removal of Omega chrome red from aqueous solution by adsorption on a homogenous mixture of fly ash and coal in different proportions under varying conditions of adsorbate concentrations, particle size of adsorbents, temperature, and the medium used. Fly ash has good capacity for removal of Methyl violet from wastewater[171]. Singh et al[172] studied the sorption capacity of fly ash and impregnated fly ash for the removal of phenol. Fly ash used as an effective adsorbent for the adsorption of 2,4,6 trinitrophenol[173]. Bagasse fly ash exhibits good sorption capacity for T.N.P. and the adsorption data follows both Langmuir and Freundlich models[174]. The sorption efficiency of the material decrease in the presence of some cleaning agents. Gupta et al[175]

has used bagasse fly ash for the removal and recovery of phenol and p-nitrophenol.

Some workers have studied on sulphonated coal for the removal of dyes[176]. Treated and untreated bituminous coal have capacity for the removal of heavy metals from waste water[177]. A comparative study for colour removal from pulp and bleach plant effluent using fly ash, lime and high molecular weight amine (Kemamine T, 1902D) as adsorbents was carried out by Gupta and Bhattacharya[178]. Results indicated that colour removal by amine was very high, but it was costlier than the treatment with fly ash, which gave 94% removal. Karthikeyn[179] used the red soil(R .S), Fly ash(F.A), Ground nut shell powder(G.N.S.P.) bauxite(B.T) for the treatment of water containing Saranine and Congo Red dye. The adsorption capacity were found as B.T > R.S > F.A >G.N.S.P for the removal of Congo red and R.S. > B.T.> G.N.S.P > F.A for Safranine. Certain low cost materials like fly ash, coal, wollastonite, and china clay were applied in the treatment of hazardous dye house wastewater rich in Omega chrome fast

blue[180]. The uptake of dye follows the order fly ash > coal > wollastonite > china clay.

Spent bleaching earth a montmorillonite mineral, is used extensively to remove trace metals, chlorophyll, cartenoids, soap residues, residues of phosphorous compounds and peroxides in palm oil industries. Pollard et al[181] investigated the adsorption of chlorophenol from aqueous solution by spent bleaching earth. Spent bleaching earth has been used for the removal of Cr (III)[182] and dyes[183] from wastewater. Hexane Spent Bleaching Earth (HSBE) employed for the removal of some organic dyes by some workers[28]. They investigated that HSBE is a better sorbent for basic dye than acid dyes. This is probably due to negatively charged surface of HSBE, which has higher affinity for cationic dyes molecules. Kun-She Low et al[184] used spent bleaching earth for decolourisation of crude palm oil. The experimental results indicate that treatment of spent bleaching earth with 10% H_2SO_4 at 350^0C produce a material, which was most effective in removing colour pigments from crude palm oil. The sorption process studied include, initial concentration, sorbent quantity and

temperature. Applicability of both Freundlich and Langmuir isotherms indicates that both physio-sorption and chemi-sorption were involved in the sorption process.

Investigators used peat as effective adsorbent for the removal of acid dye (Telon Blue)[185]. Several workers reported the removal of chromium by unconventional adsorbents like peat moss[186], lignite[187] and pyrite cinders[188]. Chaney et al[189] used peat moss for the adsorption of cadmium ions from wastewater. Oka and coworkers[190] suggested the use of sulphonated peat and humic acid for the removal of Hg (II) and reported that the presence of foreign metal ions had little effect on removal efficiency. Adsorption of acid dyes[191] and basic dyes[192] on peat from single and multi-component system has been reported by some workers. For basic dyes, they have applied Freundlich, Langmuir, and Redilich Peterson isotherm equations. The adsorption of Basic yellow-21 from aqueous solution on peat has been also examined by Allen et al[193]. Some investigators have applied peat and lignite for the removal of metal ions[194] and basic dyes[195] from wastewater and aqueous solution. Peat

activated char and lignite carried out for the removal of dyes and metal from water and NO_2 from air by Stephen et al[196].

Phenol and phenolic compound exist in wastewater from oil refineries, cake plants, phenolic resin plants and so on. Phenol can cause bad taste and odour in drinking water even at low concentration. The injection of such contaminated (with phenol) water in human body cause protein degeneration, tissue erosion, tumour and paralysis of C.N.S(central nervous system) and also damage the kidney, liver and pancreas. So, it is necessary to remove toxic phenol and its derivatives from water.

Phenol is a weak acid and can be removed effectively from aqueous solution by anion exchange resin[197, 198]. Activated carbon has been successfully used for the removal of phenol[199, 200]. Phenol adsorb on resin in hydroxide form can be desorbed by using hydrochloric acid[201]. Activated carbon prepared from rice hulls has good capacity for the removal of substituted phenol from aqueous solution[202]. Hydrous CdS(s)[203], ZnS(s)[204], were used for the removal of phenol. Bituminous coal has also

been used for the adsorption of phenol from aqueous solution[205]. Streak et al[206] investigated the sorption capacity of conventional and novel activated carbon, made from the wood, coal, and coconut shell for the removal of phenol and parachlorophenol. It has been reported that jack wood saw dust is good adsorbent for adsorption of phenol from aqueous solution[207]. The extent removal was dependent on concentrations, pH, and temperature of the solution. The spent adsorbent can be regenerated and refused by acid treatment.

Some investigators suggested that sugar industry waste material bagasse fly ash has powerful capacity for the removal of 2,4 dinitrophenol[208]. Rong Chiwang and coworkers[209] investigated the adsorption of phenol, p-chlorophenol, p-nitrophenol, on to granulated activated carbon (GAC) in liquid-solid fluidized bed. The effect of particle size, liquid flow rate, initial phenol concentrations and activated carbon mass were investigated. Activated carbon made from carbonized slash pine bark used as an adsorbent for the removal of phenol and penta-chlorophenol[210]. In this study the Langmuir

equation provide a slightly better fit than Freundlich equation to two sets of phenol. Removal of phenol, o.m.p cresol and benzyl alcohol from their aqueous solution have been measured on activated carbon, made from silica at 278, 298 and 323K by Vijayalakshmi et al[211]. An anomalous temperature dependence of adsorption of these compounds has been observed. In this study, adsorption measurement at 278 K shows that adsorption is not reversible in the lower concentration range.

Flock and coworkers[212] carried out the purified soyabean peroxidase and raw soyabean hulls for the removal of aqueous phenol and 2-chlorophenol. Rengaraj et al[213] prepared activated carbon from palm seed coat by dolomite process. It shows the 95% removal of o-cresol from aqueous solution under optimum conditions. Recovery and regeneration of used carbon was studied in-situ and found that chemical regeneration techniques show good results. Activated carbon made from coffee groundnuts has been useful for the removal of phenol[214]. Commercial activated carbon was tested as an adsorbent for the removal of phenol from

aqueous solution by Riaz and coworkers[215]. They showed the percentage adsorption of phenol increase with the amount of activated carbon increase and also studied the adsorption of picric acid, pyrogallol and salicylic acid by activated carbon.

The derivatives of chitin and chitosan appear to be more attractive for the removal of dyes and metals. Chitosan in a partially acetylated glucosamine polymer encountered in cell wall of some fungi, such as mucosales strains. Chitosan was produced from lobster shell. It also results from de-acetylation of chitin. Chitosan has efficient capacity for the uptake of metals. Chitosan have amino group chain and can serve as chelating sites for metals. A nos. of use for chitin and chitosan in the textile industry were demonstrated in US and many countries and also bio-degradability and anti-microbial properties of these materials are well known. These are also used in medical and as component of wound dressing.

McKay et al[216] studied the adsorption of dye onto chitin. Some workers investigated natural

polymer (chitosan) generated from seafood for the removal of metals[217]. Cadmium removal efficiency of chitosan was studied by the Jha et al[218]. Chitosan has been used for the removal of anionic dyes from aqueous solution[219]. Seo and coworkers[220] examined that chitosan gel as an effective adsorbent having a hydrophobic group for the removal of Methyl orange. Chitosan and its derivatives have been utilized for the removal of uranium and vanadium metals[221]. Chitin was found to be a very good adsorbent for the removal of acid dyes from aqueous solution[222]. The effect of factors such as dosage, temperature, pH, and particle size has been studied.

Cole et al[223] studied the adsorption of phosphate and calcite. Fly ash has been used as an efficient adsorbent for the removal of phosphate from domestic water[224]. Removal of phosphate from aqueous solution by calcium carbonate and kaolinite have been studied[225]. Alumina is used for the adsorption of phosphate ions from domestic water[226, 227]. Tamarind nutshell carbon has good capacity for the adsorption of ions[228]. Soil having adsorptive power for the removal of phosphate from

aqueous solution was investigated by Parveenbalu et al[229].

The adsorption of chlorine on the surface of Ag (III) has been found to be efficient[230]. Manganese oxide has been used for the removal of Pb[231]. The adsorption increases with increase of pH because of hydrolysis of metal cation or variable change sites on MnO_2. The adsorption of methanol, formaldehyde and formic acid on Cu/ZnO and $Cu/ZnO/Cr_2O_3$ have been studied by transmission infrared Spectroscopy[232]. Gorigmin et al[233] investigated the adsorption capacity of manganese oxides for the removal of cadmium and copper ions. It has been reported that significant amount of Co, Cu, Zn, Ni, Pb, Ag and Cd in soils were associated with MnO. The interactions of dyes with metal hydrous sols and gels have been studied by number of coworkers[234, 235]. Suddhodan and coworkers suggested hydrous zirconium oxide as an adsorbent for the efficient removal of toxic heavy metals such as Hg[236], Cd[237] and Zn[21].

Sodium titanate has been used as an adsorbent for the adsorption of Ca++[20] and Zn++[238] by a

Radiotracer technique. The study comprises of various physio-chemical parameters such as concentration, temperature, pH and the effect of some added cations/anions and acid concentration (HCl/H_2SO_4) on the adsorption process. Process follows first order rate law and data fit well for a Freundlich adsorption. Barium titanate is also used for the removal of mercury ions from aqueous solution[239]. The uptake was found to increase with increasing concentration, temperature, and pH of the adsorption solution. Removal appears to be ion exchange in type and thermodynamically irreversible in nature.

Much interest has been exhibited in the use of fungal adsorbent[240], starch xanthate[241] and discarded automotive tyres[242] for the removal of cadmium from water and wastewater. Shimiza et al[243] noticed a decrease in adsorption Cr (VI) on silk fiber from aqueous solution (6 h, 25°C) with increasing pH. Metal cations were removed by using wool-carbonizing waste[244], waste rubber[245], ionic dyes[246] were adsorbed on carbonizing wool for the adsorption of ionic dyes. The removal of Cd by adsorption on water hyacinth was studied[247].

Malmary and coworkers[248] studied the removal of basic dyes from aqueous solution by using the vegetable part of carbonized wool waste as an adsorbent and observed that about 98% removal occurs in continuous mode of operation. Royer and others[249] carried out batch and continuous study for the removal of bleached kraft effluent by white rot fungus.

McKay et al[250] carried out the adsorption kinetics study of four dyes viz, Basic Blue-69, Basic Red-22, Acid Blue-25, and Acid Red-114, using bagasse pith as an adsorbent. They have considered the effect of agitation, initial dye concentration, temperature, pith mass and pith particle size. A model is developed to determine the external mass coefficient and its correlation with the above variables. Geundi et al[251] studied the adsorption of Astrazone Blue, Maxilon Red, Telon Blue and Erionyl Red on to natural adsorbent maize cob. High capacity was observed in case of Astrazone Blue and Maxilon. Maize cob has also been used for the removal of colour from textile efluents[252]. Red mud has been used as potential adsorbent for treating dying industry wastewater

rich in reactive dye[253]. The adsorption of phenol (Ph-OH), p-nitrophenol, salicylic acid, p-amino phenol from aqueous solution by various type of carbon fibers derived from hydrate cellulose was studied[254]. Oxidized anthracite has capacity to remove Zn, Cu, Cd and Pb from aqueous solution or waste water[255].

Banana pith has been used for the removal of Congo Red from aqueous solution[256]. Hydrailla verticillota carried out for the adsorption of basic dyes from wastewater[257]. Hyacinth roots are useful for the adsorption of basic dyes from waste water[258]. Osman et al[259] used the mushrooms for the removal of heavy metals. Some workers for the efficient removal of heavy metals have investigated algae cells[260] and bacteria cell[261]. Sun et al[262] used sunflower stalks for the removal of heavy metals. Sone river sand used as an adsorbent for the removal of basic dyes from aqueous solution[263]. In this study the applicability of Langmuir and Freundlich isotherms suggest the formation of monolayer cover of dye molecules on the outer surface of the adsorbent. The thermodynamics of

dye-sand system indicate spontaneous and exothermic nature of the process.

Cheng et al[264] used activated sludge for the removal of heavy metals (Pb, Cu, Cd, Ni). The specific adsorption of trace metals such as Cu, Cd, Pb by inorganic particulates such as Mn (VI) oxide, Fe (III) oxide, $Al(OH)_3$, clays and iron ores were studied by some workers[265]. Activated sludge has been used by Nelson et al[266] for the removal of Cd (II), Zn (II), and Cu (II) from waste water. Chrome sludge has been used as a best adsorbent for the removal of colour from effluents[267].

Activated carbon obtained from buffing dust, a solid waste generated in leather industry has been used for the removal of dyes from wastewater was investigated by Sekhran et al[24]. They investigated that adsorptive capacity of buffing dust(2 kg per 200 kg leather produced) based activated carbon was 6.24 mg/gm at a 3.5 pH, temperature 30^0c for dye concentration of 125mg/l and carbonization temperature 900°C. Waste bamboo dust from chipping unit was used as a sorbent for colour removal from combined effluent of the pulp and

paper mill[268] . Bamboo dust carbon was also equally effective in colour removal from the combined effluent stream at acidic pH a dose of 3.1 gm/l could remove as much as 99% colours.

Casein[269] a natural milk phospho-protein obtained by high-speed centrifugation at pH 4.6 is likely to have a great adsorption capacity for the removal of Zn^{+2}, Hg^{+2}, and Cr^{+3} from aqueous solution. In a single batch equilibrium experiment decrease in adsorption concentration (10^{-2}-10^{-8} mole/l) and increase in temperature (293-323 K) and pH (3-10) specially increased the uptake of the metal ions. Detection from thermodynamics and desorption data concluded that the uptake of those metal ions was irreversible and endothermic in nature.

Poots et al[270, 271] have reported that spruce wood is a potential adsorbent for the removal of Basic dye (Astrazone Blue) and used wood for the removal of acid dye (Telon Blue). Ramteke and coworkers[272] removed Malachite green more than 90% from wastewater by using pyrolytic char as an adsorbent. Charred plant material also used as an adsorbent for the removal of Acid Blue and Basic

Red-22 from wastewater by Perineau et al[273]. L-shaped isotherm was found to fit in this study showing monolayer adsorption of dye molecules.

Sawdust is inexpensive, it contains various compounds with polyphenolic group that might be useful for binding heavy metals. Vaishya and coworkers[274] have used sawdust for the removal of metals. Decolourisation of acidic solution of basic dye stuff (Astrazone Blue) was carried out by Asfour et al[275] by using hard wood (Beech) saw dust as an adsorbent. They observed that hard wood contain higher percentage of hemi cellulose and lignin and consequently contain more acidic group than soft wood and shows more affinity towards the adsorption of basic dyes.

The use of wood meal for the removal of Acid Blue-25 was made by some workers[276] . Sodium polysulphide treated saw dust of rubber wood exhibits a good adsorption potential for Co(II)[277]. The percentage of Co(II) adsorption increase with the increase in temperature and decrease in initial Co(II) concentration. In this study removal curves are smooth and continuous indicating the formation

of monolayer coverage of the adsorbate on the outer surface of the adsorbent. The spent sorbent can be regenerated by acid and can be reused. Removal of Methylene Blue from aqueous solution by adsorption process on cellulose-based adsorbent prepared from saw dust was studied[278]. Adsorption increases significantly with decreasing particle size and increasing dye concentration.

Some workers[279] investigated that activated carbon (raw charcoal) obtained from reeds have been used for the removal of Cu^{+2} ions from industrial wastewater and aqueous solution at 293 K. They studied that the presence of other metal ions in the solution decreases the adsorption capacity for Cu and the chemical nature of the charcoal surface and metal ions. Refused Derived Fuel (RDF) is useful by-product of solid waste. RDF is easily available and inexpensive material. RDF has good capacity for decolourization of the wastewater containing Methylene Blue[280]. In this study, intra-particle diffusion is playing an important role in adsorption process. The effect of temperature shows some chemical interaction between adsorbent/adsorbate systems with increase

in particle size and decrease in the adsorption rate. Anderson and coworker[281] did the treatment of highly coloured water by a magnetic gel. Magnetic charcoal is used for the removal of water-soluble dyes from wastewater[282].

Agricultural by product vary greatly in their ability to remove metals and dyes from solution. Recent examples of agricultural by-product are base treated rice bran, rice hulls, coconut husk, fiber, nut shell, refined corn hulls, modified peanut shell, soyabean, cotton seed hulls, rice straw, almond shell, sugar cane bagasse. Coconut husk has been used for the removal of textile dyes from aqueous solution and wastewater[283]. Olive stone was found to be good adsorbent for the removal of Pb from wastewater[284]. Activated carbon from agricultural waste like coconut husk and coconut shell prepared by some workers[285]. Coconut husk has also been used for the adsorption of cationic dye from wastewater by Low et al[286]. Activated carbon prepared from almond shell has also been applied for the adsorption of Pb from wastewater and aqueous solution[287]. Rice hulls and brans[288] are useful in the removal of metals from aqueous

solution. Tan and coworkers[289] investigated the removal of chromium (VI) on coconut husk and palm pressed fiber from aqueous solution. Verma et al[290] proposed rice bran for the adsorption of Cu (II) ions from aqueous solution.

Wayne et al[291] used six agricultural by-product of soyabean hull, cotton seed, hull, rice bran as metal adsorbent. In this study, only soybean hull, cottonseed hulls and deflated stabilized rice brans appears as a potential metal adsorbent for both synthetic and actual wastewater. Rice bran exhibited higher adsorption capacity towards Co (II), Cr (II), and Zn (II) than either of the hulls. Cotton seed hulls demonstrate the lowest adsorption capacity towards these three metal ions as well as Ni (II) and Co (II). These by-products must posseses high resistance to abrasive force in batch and column applications. Mishra et al[292] has used rice husk for the adsorption of Zn (II) ions from aqueous solution. The uptake of Zn (II) ions on rice husk (Jaya) is favoured at high temperature (293-320K) and high pH value (3.2-10.2) of the adsorptive solution. The percentage of adsorption is higher at higher dilution, obeys the first order rate

law and agree well with classical Freundlich adsorption isotherm.

Adsorption of Cr (VI) from waste water using different types of activated carbons produce from coconut shell, dust coal and wood were investigated by Selomulya and co worker[293]. Rice bran based activated carbon has efficient capacity for the adsorption of di-azo and triphenyl methane dyes from aqueous solution[294]. Better removal of dye chemicals from wastewater can be accomplished at pH (2.0-3.5) and 20-30°C. Mitchell et al[295] used agricultural by-product such as soft lignocelluloses, rice straw, soyabean hulls, sugar cane bagasse, peanut shells and harder material such as pecan and walnut shell as adsorbents for adsorbing metals and organics.

materials and methods

MATERIALS AND METHODS

Before proceeding for the detailed study, a primary investigation was undertaken. The wood was collected from the adjoining campus, washed, dried, carbonized, grind and sieved by 120 mesh and heated for activation. The activated powder of wood was taken as adsorbent: 0.2 gm of activated powder is added in dye solution at temperature of 30^0C. After ½ hour contact period, the solution was filtered and the concentrations before and after adsorption is noted spectrometrically.

Encouraged from the results of preliminary work, the detailed study was planned. In present experimental study, the wood of eucalyptus was collected from the campus of Bipin Bihari, P.G College, Jhansi. The wood was of grayish colour with rough surface. Wood was continuously washed with double distilled water to remove the dirt particles and water-soluble impurities from the surface. It was then dried and cut into small pieces by cutter.

Gupta and coworkers[296] prepared eucalyptus wood charcoal by carbonizing. The sample was carbonized under two different heating and cooling cycles namely slow and rapid. In slow carbonizing, wood is heated gradually from room temperature to pre-determined carbonization temperatures of 400, 600, 800, and 1200^{0}C at the rate of 4°Cmin^{-1}. Soaking time at these final carbonizing temperatures was 1hr and then the char sample was allowed to cool gradually at room temperature. In rapid carbonization, wood sample is heated at required carbonizing temperatures of 400, 600, 800, 1050°C at the rate of 20, 43, 80, 170°Cmin^{-1} for 1 hour respectively and then cooled at room temperature.

It was observed that slow heating rate increased the char yield, this is due to the increased resistance of volatile matter within the wood samples which allows secondary reactions to occur to much larger extent. This leads to higher carbon deposition and hence higher wood char. However, in the case of rapid carbonization the rate of volatile matters release from the wood sample was so fast that it had less opportunity to

crack and undergo the carbon deposition process before escaping from the sample. This results in the absence of any carbon deposition and thus lower char yield. Thus, it is found that with the same carbonization temperature, slow carbonization of eucalyptus wood yield char appreciably higher than that obtained by rapid carbonization.Figures[297] given below give microscopic view of chars for the various cases of eucalyptus wood:

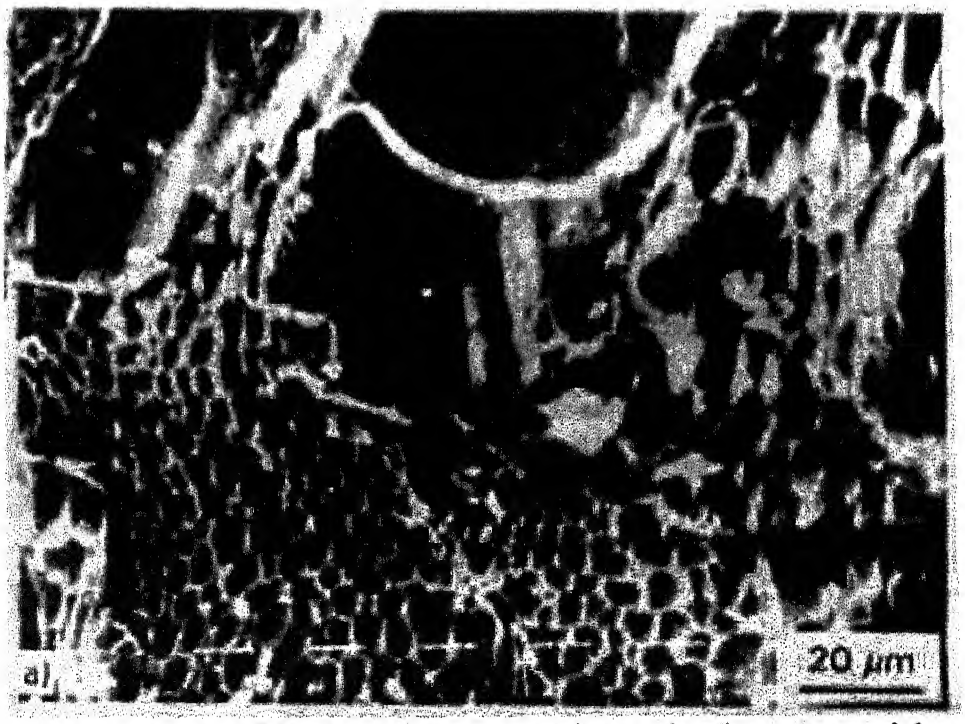


fig 1. shows SEM photographs during rapid carbonization of eucalyptus wood at 1050°C for soaking time of 1hr.

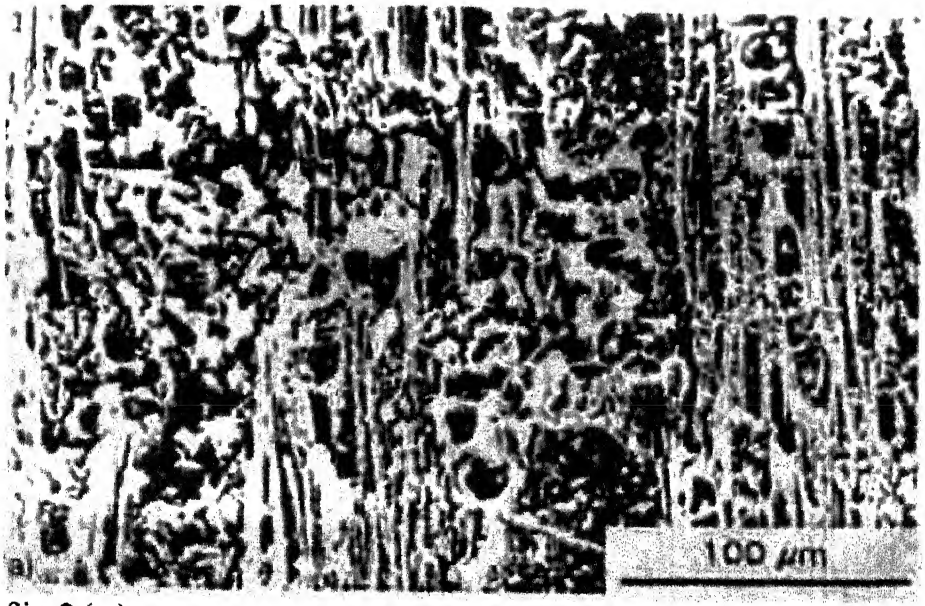


fig2(a)

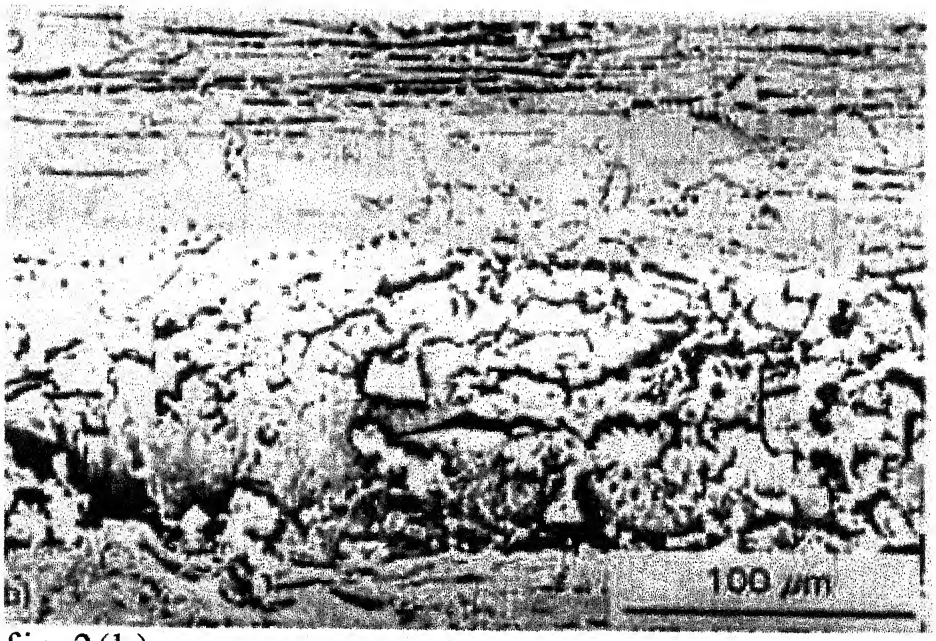


fig 2(b)

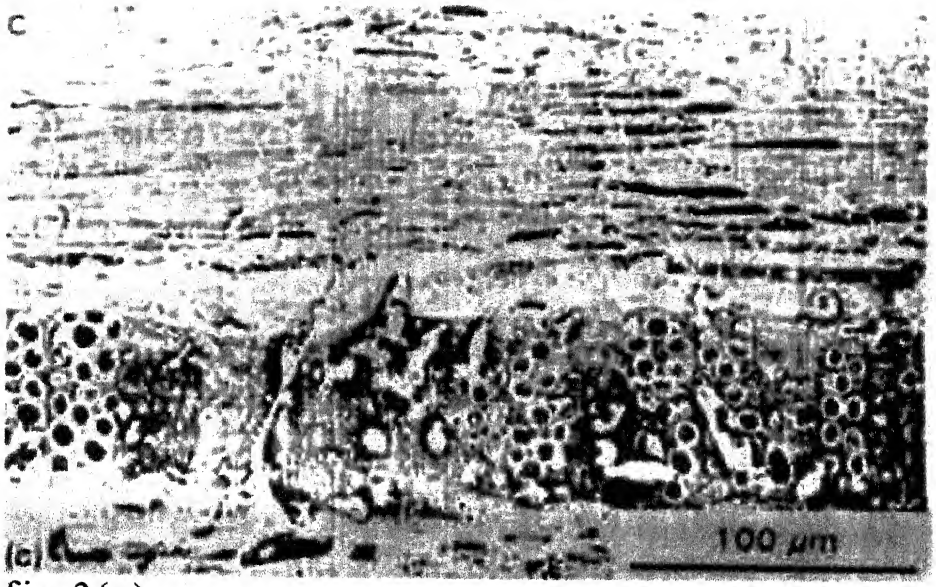


fig 2(c)

fig 2. shows various photographs of wood charcoal during rapid carbonization at 1000°C for varying soaking period of

(a) 1hr

(b) 3hr

(c) 5hr

fig 3(a)

fig 3(b)

fig 3 SEM photographs of eucalyptus wood chars prepared at 800°C during (a) rapid carbonization (b) slow carbonization for soaking time of 1hr.

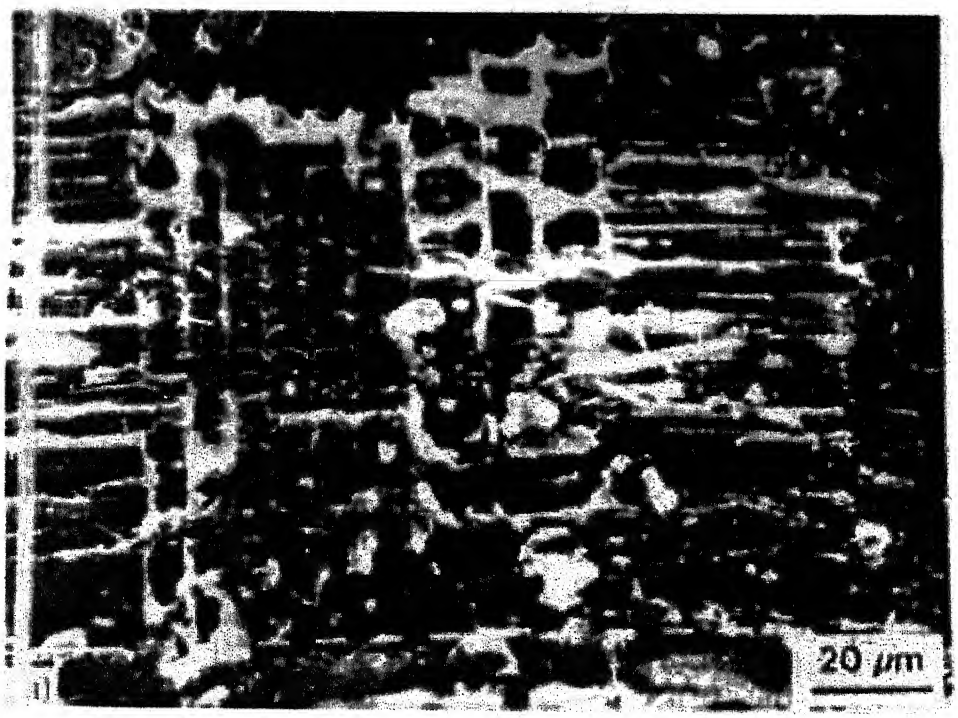


fig 4(a)

fig 4(b)

fig 4 SEM photographs of eucalyptus wood when viewed along (a)radially, (b) tangentially.

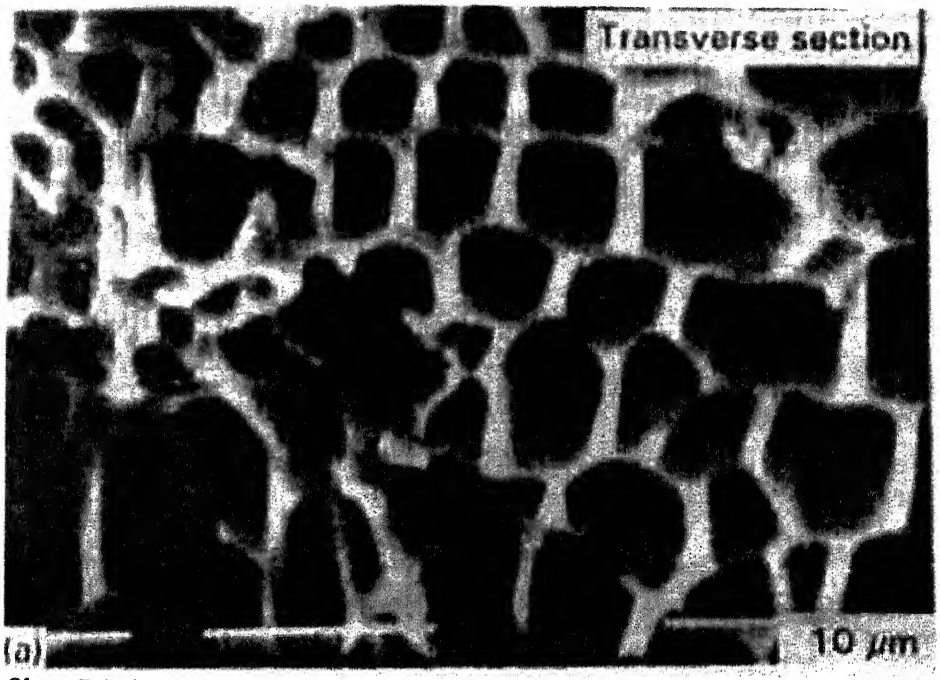


fig 5(a)

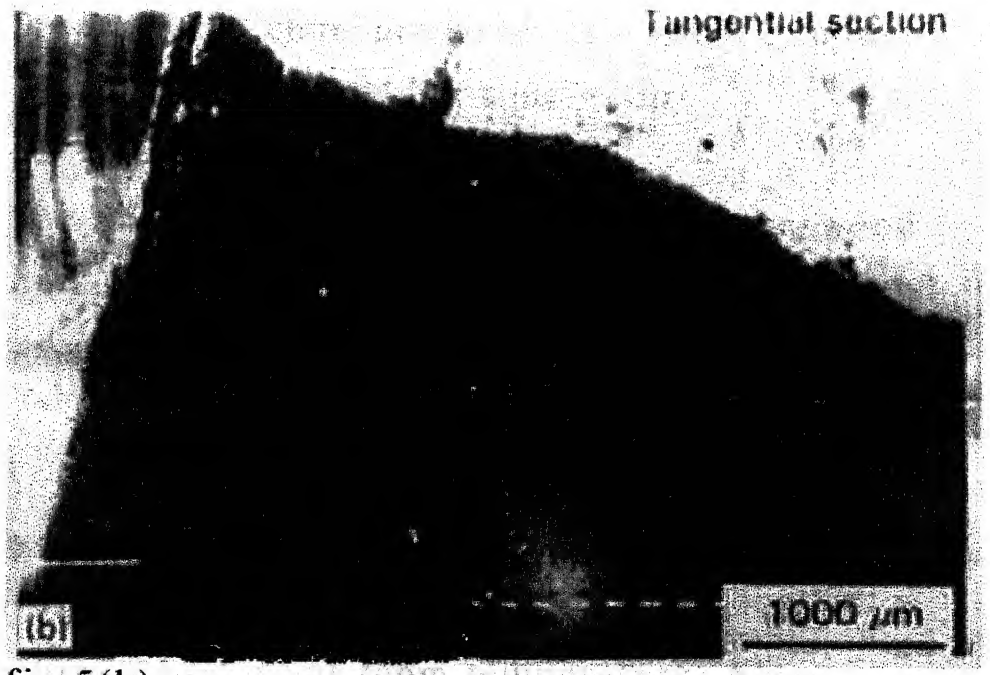


fig 5(b)

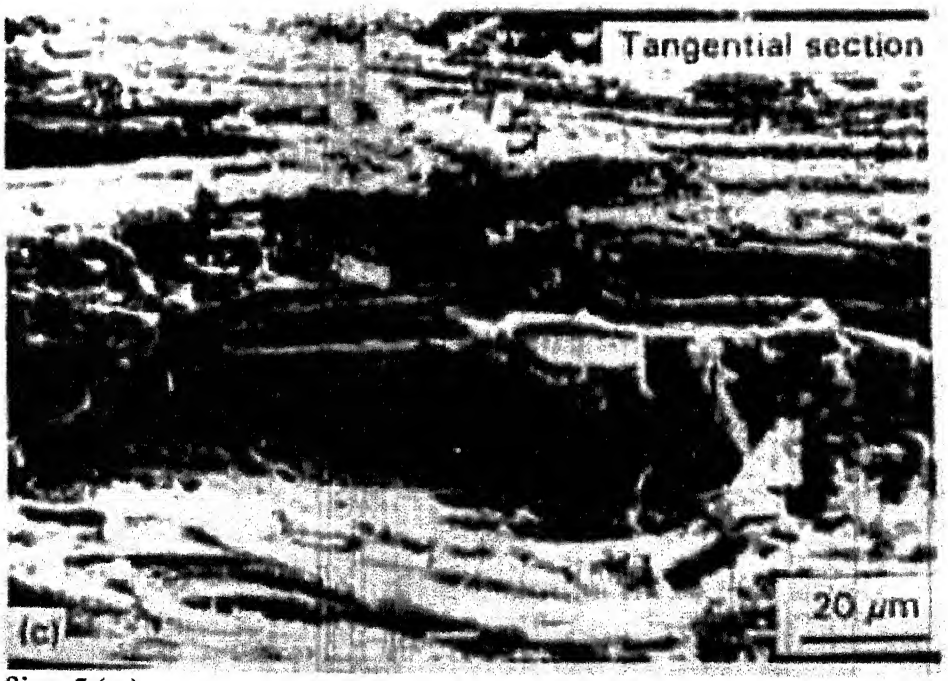


fig 5(c)

fig 5(a),(b) and (c) SEM photographs of eucalyptus wood char prepared at 1050°C under rapid carbonization. Soaking time = 1hr

The chemical composition of eucalyptus wood and their chars under slow and rapid carbonization processes was carried out[298]. Table (4)

For the preparation of char, wood pieces were slowly carbonized at 850°Cin the muffle furnace for 1hr to remove volatile matter. Then charcoal was allowed to cool at room temperature. After

Table 4 Chemical composition of Eucalyptus wood [298] and their chars produced under Slow/ Rapid Carbonization processes) (Soak Time 1hr)

Sample	Carbonization Condition			Char Yield (Wt % of dry wood)	Proximate analysis (Wt% dry basis)			Ultimate analysis (Wt% dry basis)		
	Heating Rate ($^0C\ min^{-1}$)	Temperature (^0C)	Soak Time (hr)		Volatile Matter	Ash	Fixed Carbon	C	H	N
Eucaly-ptus wood	-	-	-	-	82.44	1.17	16.39	57.20	5.25	NIL
Eucalypt us wood chars	4 (slow)	800	1	26.74	7.20	4.15	88.59	92.67	NIL	NIL
	4 (slow)	1000	1	24.50	6.60	4.40	89.00	91.50	NIL	NIL
	4 (slow)	1200	1	-	6.40	4.53	89.07	92.60	NIL	NIL
	4 (rapid)	800	1	22.58	6.80	4.40	88.80	94.35	NIL	NIL
	4 (rapid)	1000	1	20.65	6.30	4.55	89.15	92.05	NIL	NIL

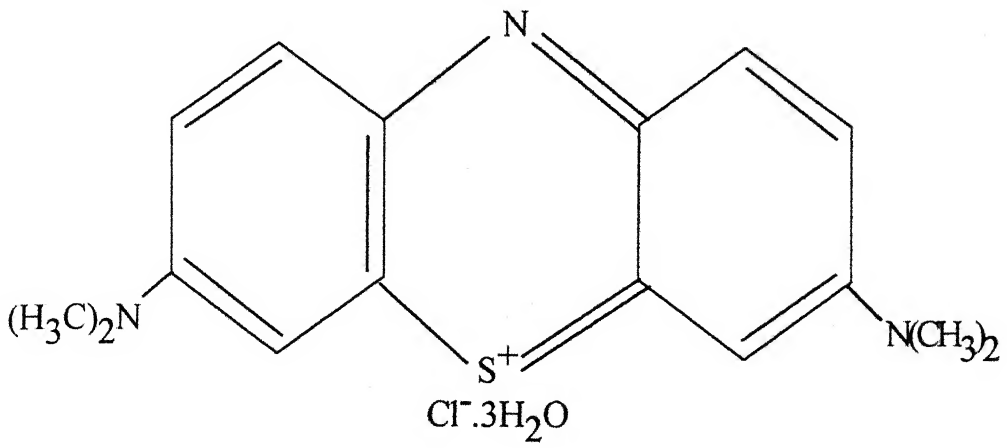
cooling, the charcoal was grind to a fine powder and then finally sieved by 150 and 180 mesh. The fine powder charcoal was activated by heating for the removal of moisture contents and then cooled to room temperature. The activated powder was then stored in desiccator at room temperature to avoid the contact of moisture into the charcoal. This activated powder was used as an adsorbent for study.

To know the adsorption capacity of the activated powder, wastewater was prepared artificially by using different coloured dyes for different colours as present in wastewater of industries. The colouring materials were all A.R. grade type of dyes. All these dyes were water soluble and easily available. The following dyes were used as adsorbate:

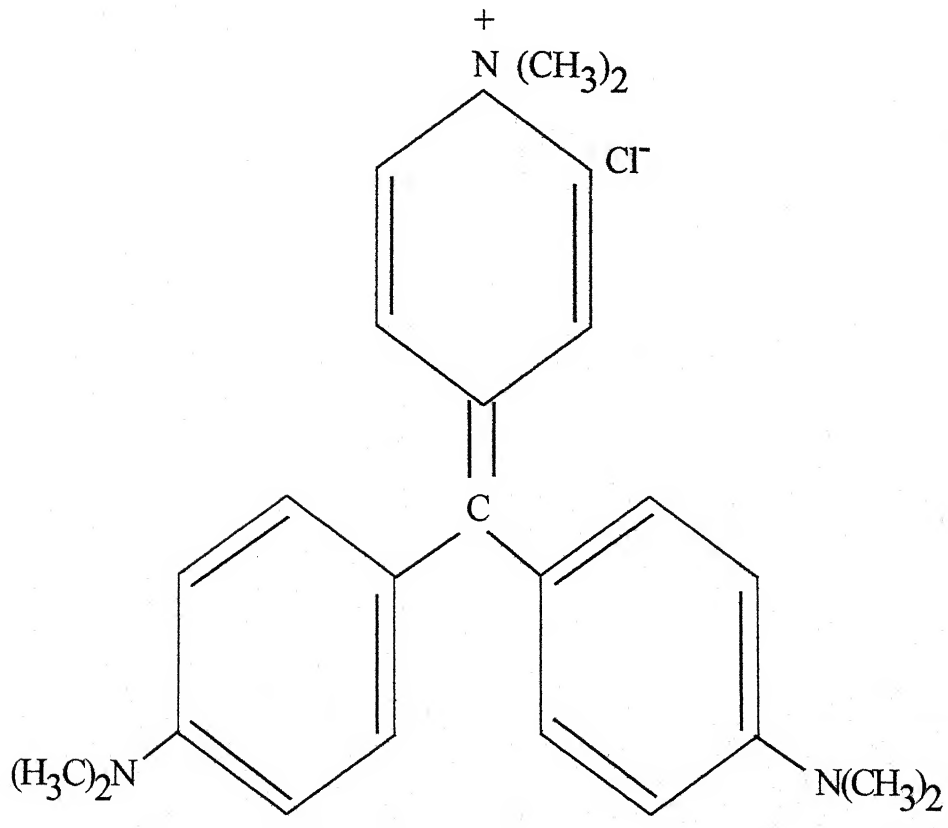
1. Methylene Blue
2. Safranine
3. Crystal violet
4. Malachite green
5. Rhodamine B
6. Aniline blue

List of chosen dye-stuff for the study :

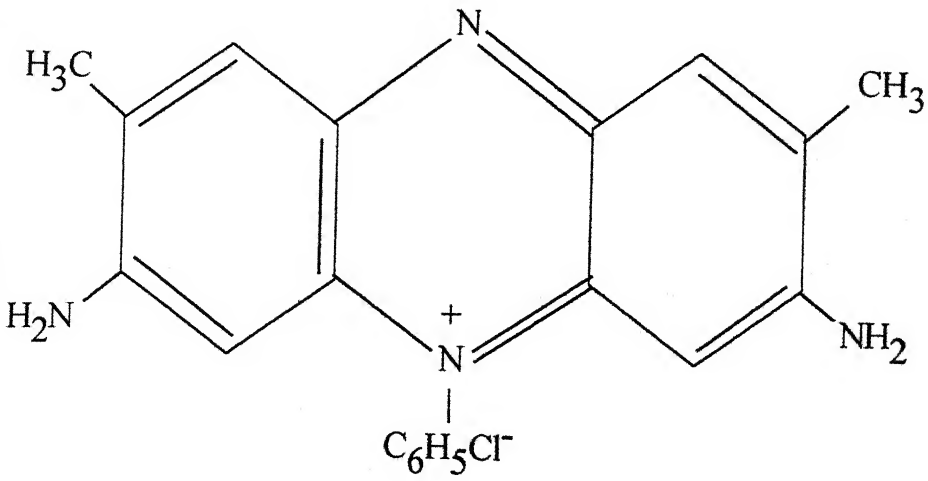
S.No.	NAME OF DYES	TYPES OF DYES	COLOUR OF DYES	NATURE OF DYES	λ_{MAX} (nm)
1	**METHYLENE BLUE**	HETEROCYCLIC DYE	GREENISH BLUE	BASIC	665-674
2	**SAFRANINE**	HETEROCYCLIC DYE	RED	BASIC	530-534
3	**CRYSTAL VIOLET**	TRI-PHENYL METHANE DYE	VIOLET	BASIC	589-594
4	**MALACHITE GREEN**	TRI-PHENYL METHANE DYE	DEEP BLUE GREEN	BASIC	590-621
5	**RHODAMINE**	XANTHENE DYE	RED	BASIC	515-524
6	**ANILINE BLUE**	TRI-PHENYL METHANE DYE	BLUE	BASIC	594-610



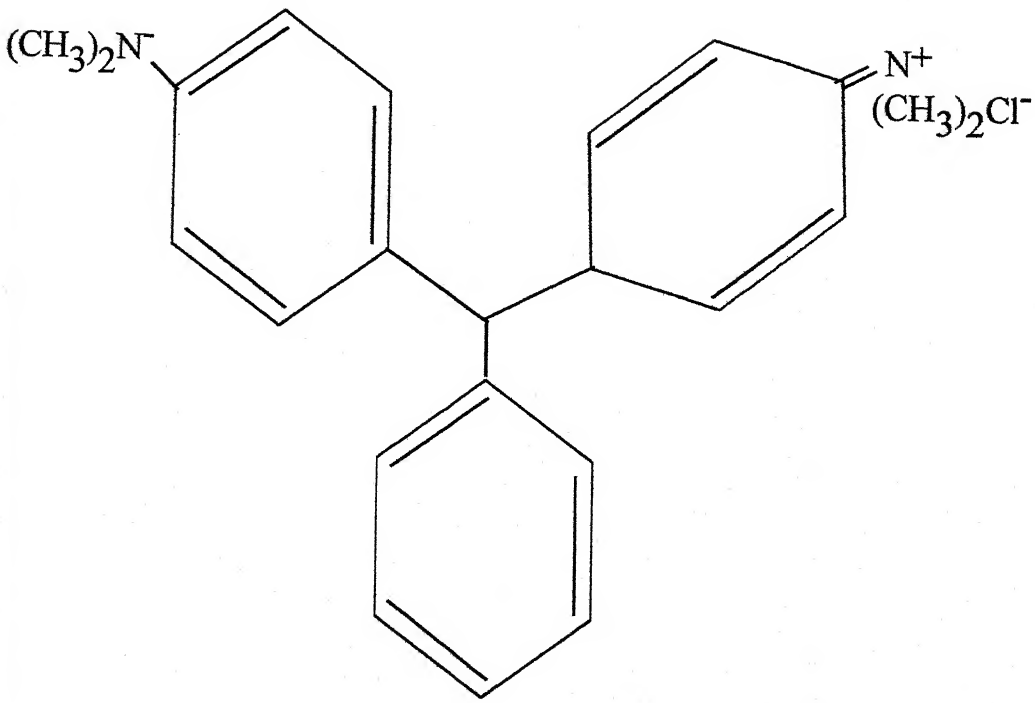
Methylene Blue



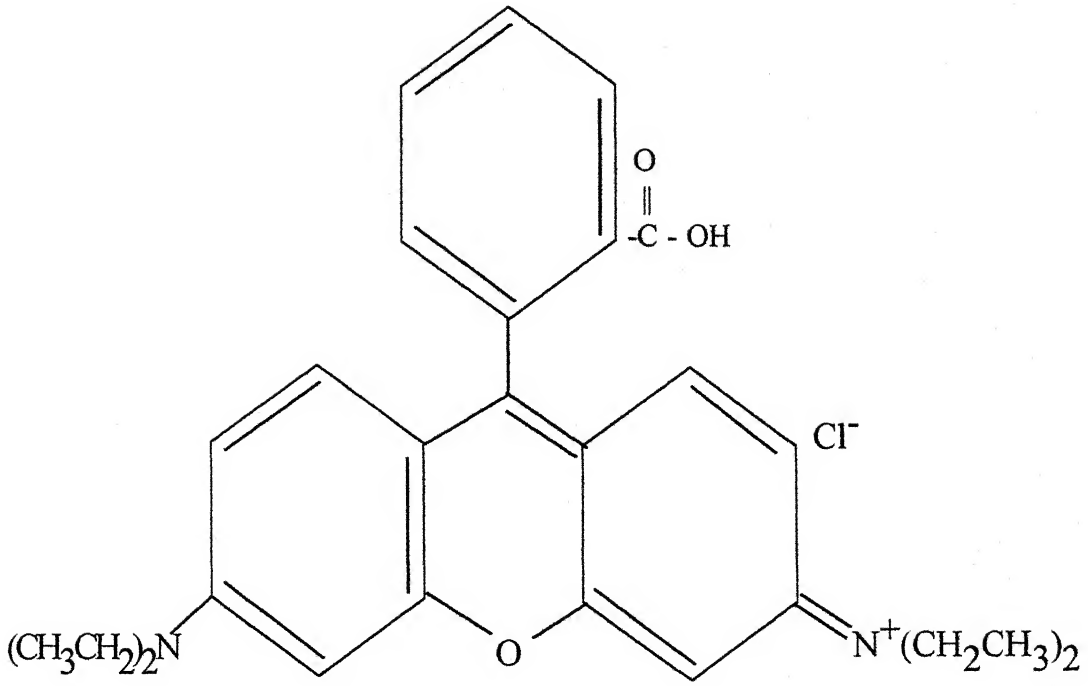
Crystal Violet



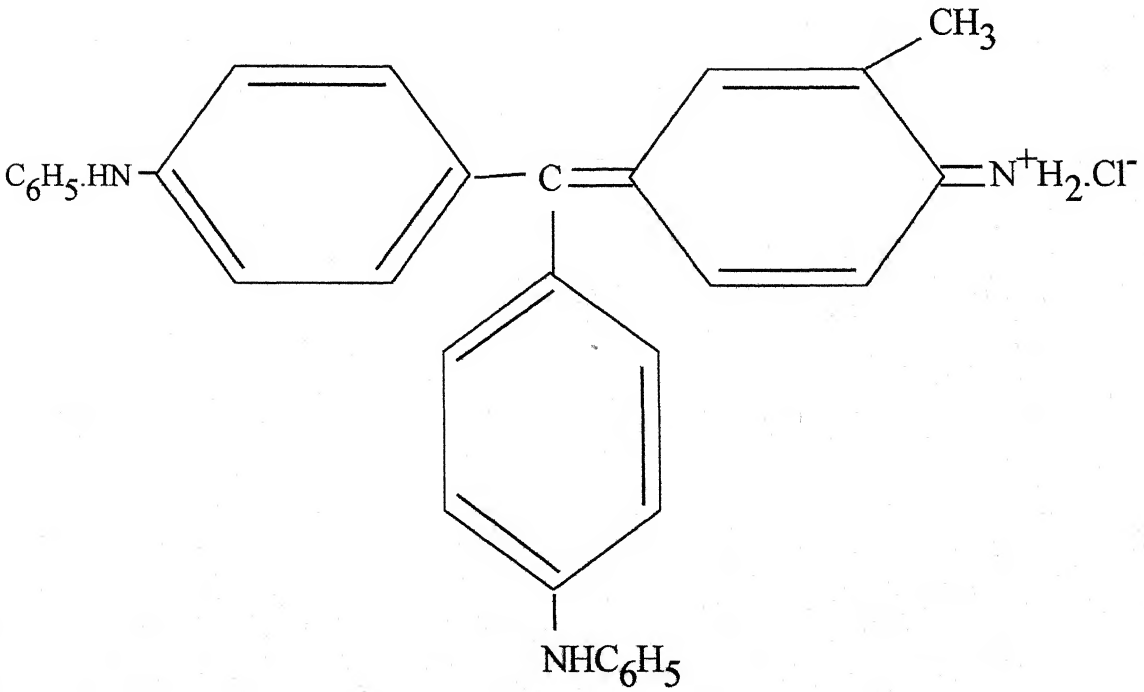
Safranine



Malachite Green



Rhodamine B



Aniline Blue

For kinetic study, all dye solution was prepared in increasing concentration of 25, 50, 75mg/l with the addition of double distilled water in conical flasks. 1 gm of activated powder was weighed accurately and added in each conical flask containing adsorbate (dye) solution of different concentration. The whole study was done at pH 7.5 and at constant temperature of 30°C. Flasks were agitated in temperature controlled rotatory mechanical shaker at uniform speed. At regular intervals of time, samples were drawn out by using syringe. The solution was filtered using Whatman filter paper42. After filtration, the concentration of the adsorbate solution was measured by Systronic spectrophotometer106 (sr no: 4113) in the visible range.

The different colouring materials (dyes) were weighed accurately. A stock solution of the concerned dye was prepared in double distilled water by dissolving weighed adsorbate in a volumetric conical flask. All dyes solution was prepared in the increasing concentration order with addition of distilled water. These dye solution were diluted to 10, 20, 30, 40, 50, 60, 70, 80, 90, and

100 mg/l respectively by addition of double distilled water.

25 ml of each dye solution in duplicate (for particle size 180 mesh) was taken into a serially arranged ten (labeled 1 to 10), thoroughly cleaned, stoppered measuring conical flask having a capacity of 100 ml for the study of the adsorption at 20°C and 30°C. Similarly, a set of ten (labeled 1 to 10), stopper conical flask containing adsorbate solutions of different concentrations were taken for the study of adsorption (for particle size 150 mesh) at temperature 20°C and 30°C.

0.2gm of activated powder of 180 mesh was weighed in a fully dried, stopper glass tube and then added into serially arranged numbered (1-10) 1 flasks containing an adsorbate solution of different concentration. Duplicate series of conical flasks were agitated in temperature controlled rotatory mechanical shakes for 30 min at a uniform speed. All particles of adsorbent were properly mixed with adsorbate solution by uniform shaking. After equilibrium, the flasks were taken from shaker and

contents were allowed to settle down. Thereafter, the solution was filtered using Whatman filter paper42. The concentration of filterates before and after adsorption was measured calorimetrically by spectrophotometer. The wavelength was selected so as obtain maximum absorbance for each dyestuff. All experiments were carried out in triplicate to achieve better results.

Adsorption is a surface phenomenon. It depends upon the surface area of the adsorbent at a given time, temperature and pressure. The extent of adsorption for the solid adsorbents increases with an increase in accessible surface area. The external area will be greater for the finer powder of the adsorbent. The size and distribution of the pores within the solid adsorbents are responsible for the accessible surface area for a given particle size. When the solid adsorbents are crushed in to smaller particles, new pores are opened and by diffusion through capillaries filled with the solvent, the adsorbate solution reach the inner surface of the porous adsorbents and thus the amount of adsorbates adsorbed will be dependent on the nature of the pores and the capillaries of the

adsorbent. Thus, the size of the particles of the adsorbents has a significant relation with their external area for their given quantity. To assess the effectiveness of adsorption by particles of eucalyptus wood charcoal, the adsorption experiment was undertaken for particle size of 150, and 180 mesh.

Adsorption dynamics:

The rate constant K_{ad} for the adsorption of dyes by eucalyptus wood charcoal at different concentration was determined by using the Lagergren equation[299]:

$\log(qe-q)=\log\{(K_{ad}/ 2.303)t\}$ where,

qe and q are the amount of dye adsorbed at equilibrium and at time t respectively.

A straight line plot of log (qe-q) Vs t indicates the applicability of the above equation. The value of K_{ad} at different concentration is calculated from the slope of the linear plots and is noted.

Analysis for thermodynamic studies:

The thermodynamic parameters obtained by the system under investigation, using equation are given in below:

$$\Delta G = -RT \ln (K)$$

$$\Delta H = -R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln (K''/K')$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T} \right)$$

where K, K′, and K″ are the equilibrium constants at different temperatures, and

ΔG = change in Gibb's free energy

ΔH = change in enthalpy

ΔS = change in entropy for the process

R = molar gas constant, and

T = absolute temperature

The observations are tabulated in the following chapter at various temperatures and other conditions as mentioned alongwith.

Study on the basis of Adsorption Isotherms:

The adsorption capacity of the adsorbent is determined by drawing equilibrium isotherms. Equilibrium isotherms give the information on the maximum amount of dye that can be adsorbed at

specified conditions. These adsorption isotherms are useful in design and development of mathematical models that describes the dynamics of adsorption. They are helpful in the determination of the adsorption capacity of various adsorbent for the removal of dye at certain temperature.

Freundlich Isotherm:

They are studied on the basis of the following equation[300]:

$(x/m) = K_f\ Ce^{1/n}$ where ,

x/m = amount of adsorbed dye

Ce = equilibrium concentration

K_f and 1/n are Freundlich constants.

Langmuir adsorption isotherm:

Langmuir adsorption isotherm model is applied for adsorption equilibrium at all temperatures and is based on the following equation[301]:

$Ce/qe = 1/Q^{\circ}b + Ce/Q^{\circ}$ where,

Ce = equilibrium concentration (mg/l)

qe = amount adsorbed at equilibrium (mg/gm)

Q° and b are the Langmuir constants related to adsorption capacity and energy of adsorption respectively.

Method for pH analysis:

To know the effect of pH on the adsorption of different dyes by eucalyptus wood charcoal the same dyes as used for the preparation of wastewater were used. The different colouring materials (or dyes) were weighed accurately. A stock solution of each dye was prepared in double distilled water by dissolving known amount of adsorbate in a volumetric conical flask. All dye solutions were prepared with for a concentration of 25mg/l. 20 ml of each dye solution was taken into serially arranged 13 (labeled 1-13) thoroughly cleaned measuring flask having a capacity of 100 ml for the study of pH effect. All studies were carried out at the temperature of 30°C. The pH of the 13 conical flasks containing dye solution (or adsorbate solution) was adjusted to 1.5, 2.5, 3.5,..... 13.5 respectively by using HNO_3 and NaOH solutions. The pH of the solution was

measured by using Systronic digital pH meter 335 (sr.no: 3218).

A 0.2gm of activated charcoal was weighed in fully dried conical flasks containing an adsorbate solution of different pH. Conical flasks were agitated in a temperature controlled rotatory mechanical shaker for 30 min with a uniform speed. All particles of adsorbent were properly mixed with dye solution by using shaker at a constant speed. After steady state is reached, the flasks were taken out from shaker and filtered using Whatman filter paper42. The concentrations of dye solutions before and after adsorption were measured by using spectrophotometer.

During the study of water and wastewater treatment by adsorption technique, the pH of the system play an important role as it affects the nature of the surface-charge of the adsorbent, extent of ionization of aqueous adsorbate species and, thus, the rate of adsorption.

The mechanism of various anionic and cationic species on such adsorbent has been

explained on the basis of competitive adsorption of H^+ and OH^- ions with adsorbate species. It is a common observation that the surface of the adsorbed anion favourable for adsorbtion at low pH due to the association of H^+ ions with surface of the adsorbent, whereas at high pH, due to the deposition of OH^- ions, the surface becomes active for the adsorption of cations.

In the present study, the influence of pH on the adsorption of dyes has been studied in order to find out a suitable pH for maximum removal. The observation has been tabulated and graphically analysed in next chapter.

Observations and results

OBSERVATIONS AND RESULTS

In this study we examined the adsorption properties of eucalyptus wood charcoal. The effect of different parameters on adsorption of various dyes using wood charcoal as an adsorbent was investigated.

1. Effect of Contact Time: -

To examine the effect of contact time on adsorption of different dyes on eucalyptus wood charcoal at 30^0C and pH 7.5 was undertaken and the value of K_{ad} was determined by using Lagergren equation.

2. Effect of Concentration: -

The concentration plays a major role in determination of the extent of adsorption. carbon has a fixed capacity for adsorption at a particular initial dye concentration and so, the volume of the solution that can be treated with a fixed amount of activated carbon depends upon the initial concentration of the dye.

3. Effect of particle size: -

The effect of particle size on concentration

of dyes was studied on different particle sizes of 150 and 180 mesh.

4. Effect of temperature: -

To examine the effect of temperature on adsorption of dyes at different temperatures namely 20^0C and 30^0 C was studied. The effect of temperature on free energy was also studied.

5. Adsorption Isotherm: -

This study was done on the basis of Freundlich's isotherm. The adsorption behaviour of different dyes on eucalyptus wood charcoal at two different temperatures was in close agreement with the linear form of Freundlich's equation.

$$\ln(x/m)=\ln K_f+(1/n)\ln Ce$$

the intercept $\ln K_f$ was roughly an indicator of an adsorption capacity and the slope, 1/n, an adsorption intensity.

6. Effect of pH on adsorption: -

In present study, the effect of pH on adsorption of dyes by eucalyptus wood charcoal was studied. The effect of initial pH of dyes solutions were studied on Methylene blue, Safranine, Crystal violet, Malachite green, Rhodamine B and Aniline blue with other

parameters kept constant. The effect of initial pH of dyes solution ranging from 2.5 to 11.5 on adsorption was studied on six different dyes at temperature 30^0C and concentration 25 mg/l.

METHYLENE BLUE

Keeping the temperature constant at 30^{0}C and pH 7.5 in whole study, when the initial dye concentration was 25mg/l the adsorption of Methylene blue on eucalyptus wood charcoal were found to be 90.00, 91.20, 92.40, 93.20, 94.40, 95.60, 96.00, 96.80, 97.20, and 97.50 with the increasing contact time of 5,10,20.....90 min respectively and with the initial dye concentration of 50 mg/l percent adsorption of dye were 86.60, 87.80, 89.00, 91.60, 92.40, 93.00, 93.60, 94.00, 94.40, 94.80 with the increasing contact time of 5,10,20....90min. Similarly, for initial dye concentration of 75 mg/l the percent adsorption were found to be 81.73, 83.33, 84.80, 86.80, 88.88, 89.86, 90.80, 91.33, 92.00 and 92.40 with thc increasing contact time of 5,10,20.....90min respectively (table 5).

Effect of contact time: -

Fig (1) showed the effect of dye concentration on the extent of adsorption as a function of time for the initial dye concentration of 25,50,75 mg/l. It was showed from fig(1) that the amount of dye adsorbed increased from 22.5 to 24.4, 43.3 to 47.4, 61.3 to 69.3 mg/gm for the initial dye

Table 5. Kinetic study of Methylene blue on eucalyptus wood charcoal at different concentration and pH=7.5 and T=30°C

s	time	initial concentration of dye		initial concentration of dye		initial concentration of dye	
no.	(min)	(25 mg/l)		(50 mg/l)		(75 mg/l)	
		amount adsorbed	% adsorption	amount adsorbed	% adsorption	amount adsorbed	% adsorption
		(mg/gms)		(mg/gms)		(mg/gms)	
1	5	22.5	90.0	43.3	86.6	61.3	81.7
2	10	22.8	91.2	43.8	87.8	62.5	83.3
3	20	23.1	92.4	44.5	89.0	63.6	84.8
4	30	23.3	93.2	45.8	91.6	65.1	86.8
5	40	23.6	94.4	46.2	92.4	66.6	88.9
6	50	23.9	95.6	46.5	93.0	67.4	89.8
7	60	24.0	96.0	47.2	93.6	68.1	90.8
8	70	24.3	96.8	47.0	94.0	68.5	91.3
9	80	24.3	97.2	47.2	94.4	69.0	92.0
10	90	24.4	97.6	47.4	94.8	69.3	92.4

concentration of 25,50 and 75 mg/l respectively with the increase of contact time and attained equilibrium in 90min at temperature of 30^0C and pH 7.5, however, afterwards no significant change was found. The time variation curves of adsorption were found to be smooth and continuous.

Adsorption dynamics: -

The straight line plots of log (qe-q) versus t for Methylene blue adsorption on eucalyptus wood charcoal at 30^0C (fig2) indicated the applicability of Lagergren equation. The value of rate constant (K_{ad}) were $2.75x10^{-2}$, $3.54x10^{-2}$, $3.17x10^{-2}$ min^{-1} ,for an initial concentration of 25,50,75 mg/l, respectively at temperature 30^0C and pH 7.5. The plot was linear for a wide range of concentration and contact period.

The adsorption of Methylene blue on eucalyptus wood charcoal (particle size 180 mesh) at temperature 20^0C were 97.00, 94.50, 94.33, 92.75, 91.00, 89.16, 88.28, 85.00, 84.11 and 82.40 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}(table 6a). The corresponding values of free energy ($-\Delta G$) were 8.687, 7.185, 7.111, 6.501, 5.965, 5.506, 5.312, 4.700, 4.557, 4.304$kJmole^{-1}$(table 7). At

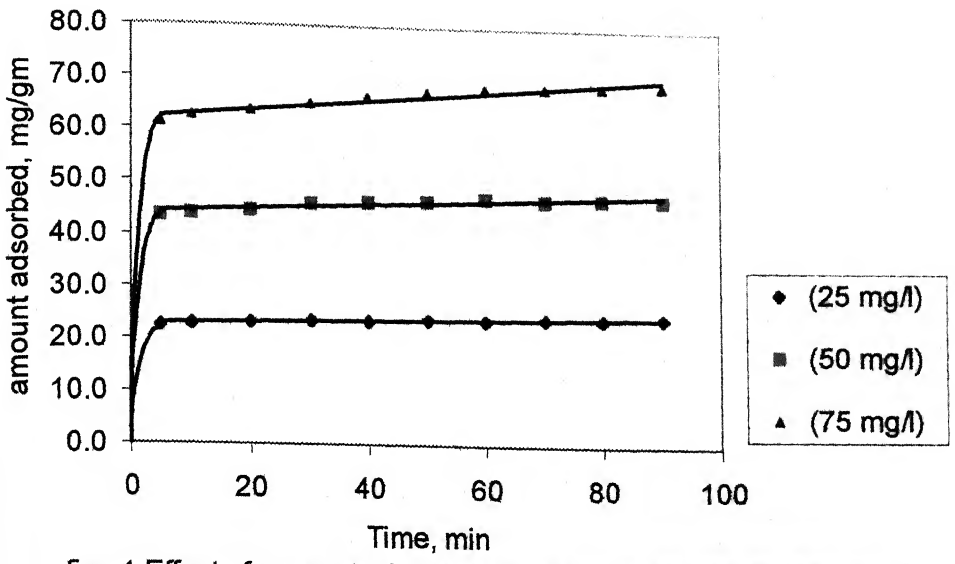


fig : 1 Effect of concentration on adsorption of Methylene blue by eucalyptus wood charcoal at pH=7.5 and T=30°C

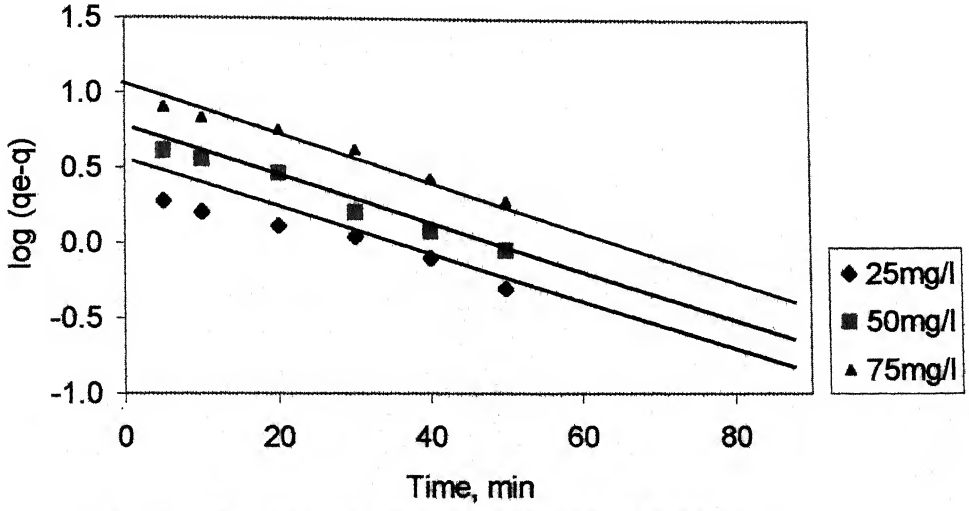


fig 2. Lagergren plot for Methylene blue adsoprtion

Table 6 Adsorption of Methylene Blue dye on Eucalyptus wood charcoal
(Particle size 180 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/L)	Equilibrium dye concentration ($1x10^{-4}$ mg/L)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.3	9.7	97.00
2	20	1.1	18.9	94.50
3	30	1.7	28.3	94.33
4	40	2.9	37.1	92.75
5	50	4.5	45.5	91.00
6	60	6.5	53.5	89.16
7	70	8.2	61.8	88.28
8	80	12.0	68.0	85.00
9	90	14.3	75.7	84.11
10	100	17.6	82.4	82.40

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/L)	Equilibrium dye concentration ($1x10^{-4}$ mg/L)	Amount of dye adsorbed (mg/0. 2 gm)	% Adsorption
1	10	0.48	9.52	95.20
2	20	1.6	18.4	92.00
3	30	2.4	27.6	92.00
4	40	3.9	36.1	90.25
5	50	5.9	44.1	88.20
6	60	8.3	51.7	86.16
7	70	10.1	59.9	85.57
8	80	13.9	66.1	82.62
9	90	16.0	74.0	82.22
10	100	18.7	81.3	81.30

temperature 30^0C, the percent adsorption of Methylene blue were 95.20, 92.00, 92.00, 90.25, 88.20, 86.16, 85.57, 82.62, 82.22, and 81.30 for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mg/l^{-1} (table 6b). The corresponding values of free energy ($-\Delta G$) were 7.775, 6.467, 6.467, 5.961, 5.472, 5.065, 4.957, 4.481, 4.422, and 4.293 $kJmole^{-1}$(table 7). The respective values of enthalpy ($-\Delta H$) were 91.18, 71.82, 64.42, 54.02, 49.34, 44.10, 35.53, 21.86, 13.46 and 10.60 $K^{-1}J$ $mole^{-1}$ (table 7). The values of K were 33.30, 18.16, 17.63, 13.78, 11.10, 9.22, 8.53, 6.66, 6.29, 5.67(table 7) in the same order of increasing initial dye concentration.

For particle size 150 mesh, the adsorption of Methylene blue at temperature 20^0C were 96.00, 95.00, 93.66, 90.50, 89.60, 86.83, 86.00, 83.62, 82.66 and 81.90 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 8a).

The corresponding values of energy ($-\Delta G$) were 7.974, 7.421, 6.836, 5.831, 5.607, 5.023, 4.871, 4.482, 4.341, 4.234$kJmole^{-1}$ (table 9). At temperature 30^0C, the percent adsorption were 93.90, 92.50, 91.00, 87.25, 86.40, 83.50, 83.00,

Table 7 Thermodynamic Parameters of Methylene Blue dye (Particle size – 180 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	8.687	7.775	35.86	91.18	33.30
2	7.185	6.467	28.59	71.82	18.16
3	7.111	6.467	26.31	64.42	17.63
4	6.501	5.961	22.60	54.02	13.78
5	5.965	5.472	20.67	49.34	11.10
6	5.506	5.065	18.65	44.10	09.22
7	5.312	4.957	15.90	35.53	08.53
8	4.700	4.481	11.21	21.86	06.66
9	4.557	4.422	08.57	13.46	06.29
10	4.304	4.293	04.62	10.60	05.67

Table 8

Adsorption of Methylene Blue dye on Eucalyptus wood charcoal (Particle size 150 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.4	9.6	96.00
2	20	1.0	19.0	95.00
3	30	1.9	28.1	93.66
4	40	3.8	36.2	90.50
5	50	5.2	44.8	89.60
6	60	7.9	52.1	86.83
7	70	9.8	60.2	86.00
8	80	13.1	66.9	83.62
9	90	15.6	74.4	82.66
10	100	18.1	81.9	81.90

(b)At Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.61	9.39	93.90
2	20	1.5	18.5	92.50
3	30	2.7	27.3	91.00
4	40	5.1	34.9	87.25
5	50	6.8	43.2	86.40
6	60	9.9	50.1	83.50
7	70	11.9	58.1	83.00
8	80	15.4	64.6	80.75
9	90	17.7	72.3	80.33
10	100	19.8	80.2	80.20

80.75, 80.33, and 80.20 for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}(table 8b). The corresponding values of free energy ($-\Delta G$) were 7.162, 6.632, 6.166, 5.274, 5.108, 4.613, 4.537, 4.219, 4.164, and 4.147 $kJmole^{-1}$ (table 9). The respective values of enthalpy ($-\Delta H$) were 32.20, 30.94, 26.81, 22.45, 20.47, 17.22, 14.81, 12.34, 9.63, 6.85$kJmole^{-1}$ and entropy ($-\Delta S$) values were 81.29, 78.92, 67.02, 55.76, 49.87, 40.92, 33.35, 26.36, 17.77, and 8.77$K^{-1}Jmole^{-1}$ (table 9). The values of K were 24.97, 19.97, 15.77, 10.51, 9.60, 7.59, 7.13, 6.10, 5.76, and 5.52 (table 9) in the same order of increasing initial dye concentration.

Effect of concentration: -

The results showed (table 6a and 6b) that the adsorption of Methylene blue decreased from 97.00 to 82.40 % by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 180 mesh) and at temperature 30^0C adsorption decreased from 95.20 to 81.30 % by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The nature of curves at both temperatures showed an increased in amount of dye adsorbed on increase in dye concentration (fig 3)

Fig showing eqm. Conc.

Table 9 Thermodynamic Parameters of Methylene Blue dye (Particle size – 150 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	8.687	7.775	35.86	91.18	33.30
2	7.185	6.467	28.59	71.82	18.16
3	7.111	6.467	26.31	64.42	17.63
4	6.501	5.961	22.60	54.02	13.78
5	5.965	5.472	20.67	49.34	11.10
6	5.506	5.065	18.65	44.10	09.22
7	5.312	4.957	15.90	35.53	08.53
8	4.700	4.481	11.21	21.86	06.66
9	4.557	4.422	08.57	13.46	06.29
10	4.304	4.293	04.62	10.60	05.67

The both curves were found to be smooth and continuous in nature.

The results showed (table 8a and 8b) that the adsorption of Methylene blue decreased from 96.00 to 81.90 % by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 150 mesh) and at temperature 30^0C,adsorption decreased from 93.90 to 80.20 % for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The nature of curves at both temperatures showed an increased in amount of dye adsorbed on increase in dye concentration (fig 4). The both curves (at 20^0C and 30^0C) were found to be smooth and continuous in nature.

Effect of Particle size: -

The results showed (table 8a and 6a) that the adsorption of Methylene blue increased from 81.90 to 96.00% to 82.40- 97.00% with decrease in particle size 150-180 mesh at temperature 20^0C. At temperature 30^0C (8b and 6b) results showed that the adsorption increased from 80.20-93.90% to 81.30-95.20% with decrease in particle size 150-180 mesh. It was observed that adsorption increased with decrease in particle size.

Effect of temperature: -

The results indicated (table 6a and 6b) that the adsorption of Methylene blue decreased from 97.00-82.40% to 95.20-81.30% with increasing temperature 20^0C to 30^0C for particle size 180 mesh. For particle size 150 mesh, results (table 8a and 8b) indicated that the percent adsorption of Methylene blue decreased from 96.00-81.90% to 93.90-80.20% with increasing temperature 20^0C to 30^0C. It was observed that adsorption decreased with the rise of temperature.

It was found that free energy ($-\Delta G$) decreased from 8.687-4.304 to 7.775-4.293 $kJmole^{-1}$ with the increasing temperature 20^0C to 30^0C for particle size 180 mesh (table 7) and for particle size 150 mesh (table 9) free energy ($-\Delta G$) decreased from 7.974-4.234 to 7.162-4.147$kJmole^{-1}$ with the increasing temperature 20^0C to 30^0C. The values of entropy ($-\Delta S$) and enthalpy (ΔH) changes were found to be negative (table 7,9).

Adsorption Isotherm: -

The results favoured the adsorption of Methylene blue on eucalyptus wood charcoal at different temperatures obeyed Freundlich adsorption

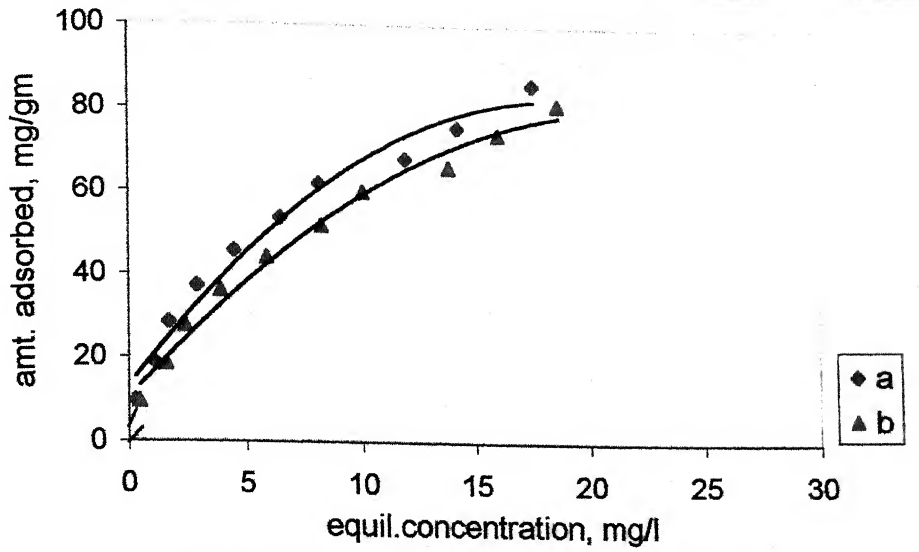


fig 3 equilibrium isotherm of Methylene blue
(Particle size 180 mesh) a - 20°C, b - 30°C

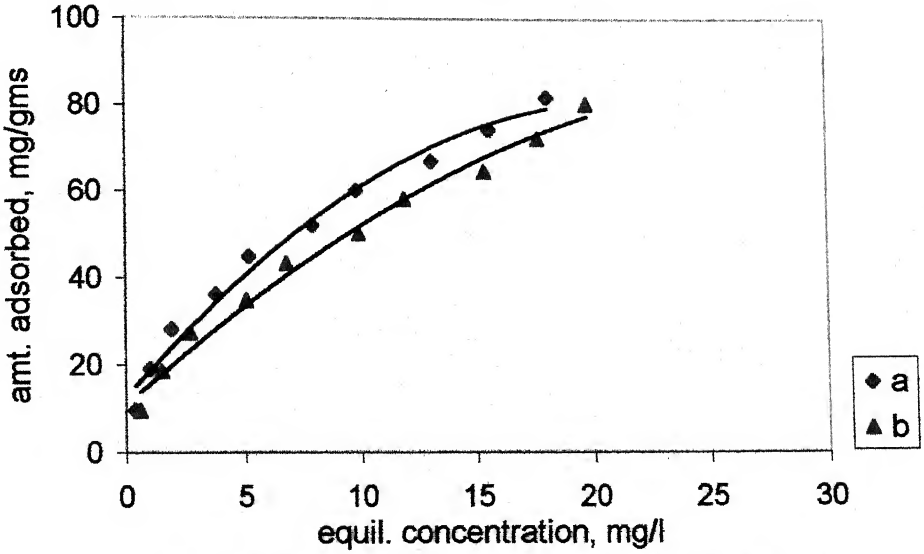


fig 4 equilibrium isotherm of Methylene Blue
(Particle size 150 mesh) a - 20°C,b - 30°C

Isotherm. The data were found fit to the linear form of Freundlich equation:

$$\ln qe = \ln K_f + (1/n) \ln Ce$$

The plot of ln qe versus ln Ce for various initial concentration was found to be linear indicating the applicability of Freundlich adsorption isotherm for particle size 180 mesh at 20^0C the values of K_f and 1/n were 2.90, and 0.554 respectively. Similarly, at 30^0C the values of K_f and 1/n were 2.71 and 0.575 for particle size 150 the values of K_f and 1/n at 20^0C were 2.79 and 0.563 respectively. Similarly, at 30^0C the values of K_f and 1/n were 2.51 and 0.607 respectively. It was clear from (table 11) that value of K_f decreased with the rise of temperature showing that the rate of adsorption decreased with the rise of temperature.

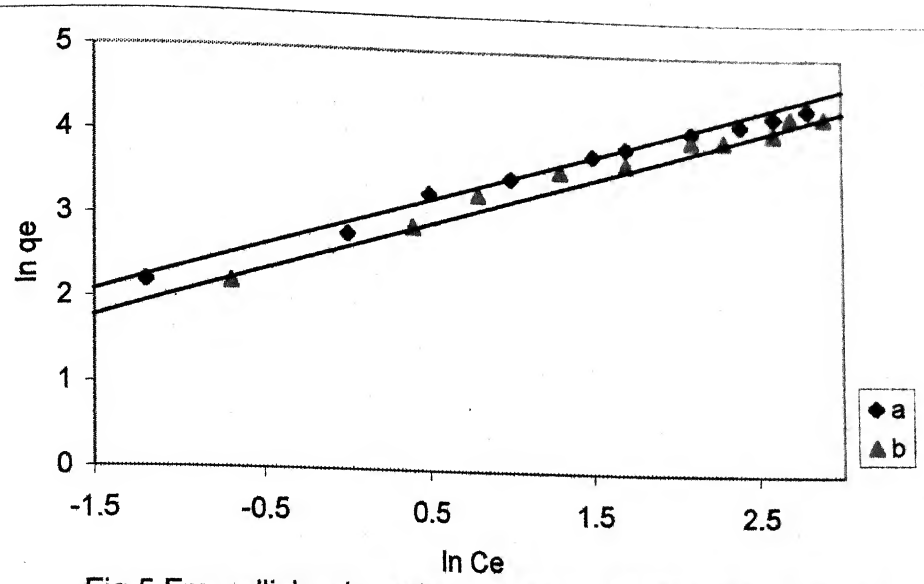


Fig 5 Freundlich adsorption isotherm of Methylene Blue a-20 °C b-30 °C (Particle size 180 mesh)

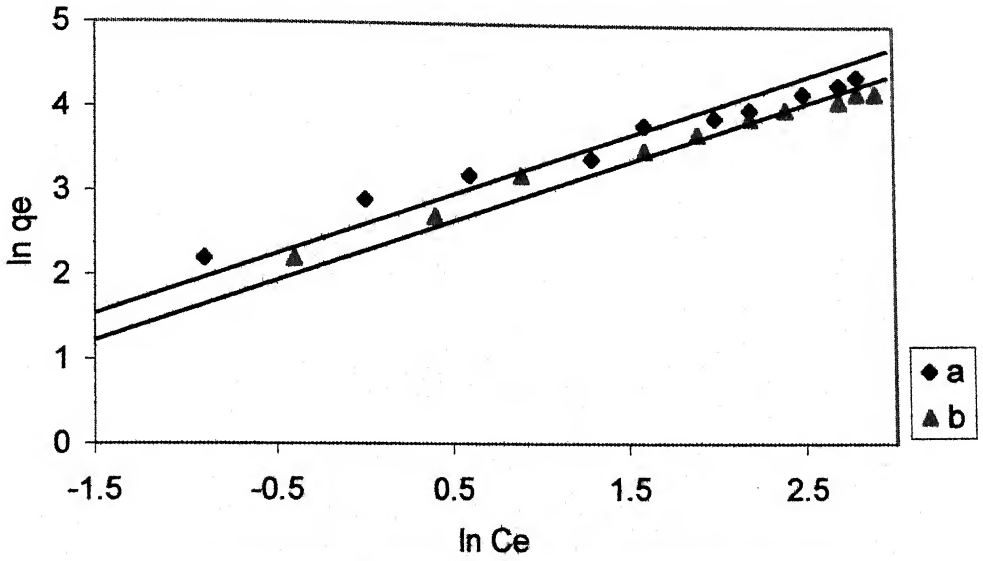


Fig 6 Freundlich adsorption isotherm of Methylene Blue a-20 °C b-30 °C (Particle size 150 mesh)

Effect of pH :-

The effect of pH on adsorption of Methylene blue dye showed in fig 7. The percent adsorption of Methylene blue were 39.60, 46.00, 51.60, 62.40, 79.20, 84.80, 87.60, 95.20, 97.20, and 91.60 with the increasing pH values from 2.5 to 11.5 at temperature 30^0C and concentration 25 mg/l (table 10). It was observed that with the increased of pH 2.5 to 10.5 the adsorption of Methylene blue increase from 39.60 to 97.20% by eucalyptus wood charcoal and for the pH above 10.5 the adsorption was found to decrease gradually (table 10).

Table 10

Adsorption of Methylene Blue at different pH , temperature 30 °C,, Initial dye concentration 25 mg/l

S No	pH	Equilibrium dye concentration (mg/l)	Amount of dye adsorbed (mg/gm)	% adsorption
1	2.5	15.1	9.9	39.60
2	3.5	13.5	11.5	46.00
3	4.5	12.1	12.9	51.60
4	5.5	9.4	15.4	62.40
5	6.5	5.2	19.8	79.20
6	7.5	3.8	21.2	84.80
7	8.5	3.1	21.9	87.60
8	9.5	1.2	23.8	95.20
9	10.5	0.7	24.3	97.20
10	11.5	2.1	22.9	91.60

Table11

Freundlich Constant for Methylene Blue

Particle Size	Temperature	K_f	1/n
180 Mesh	20^0 C	2.90	0.554
	30^0 C	2.71	0.575
150 Mesh	20^0 C	2.79	0.563
	30^0 C	2.51	0.607

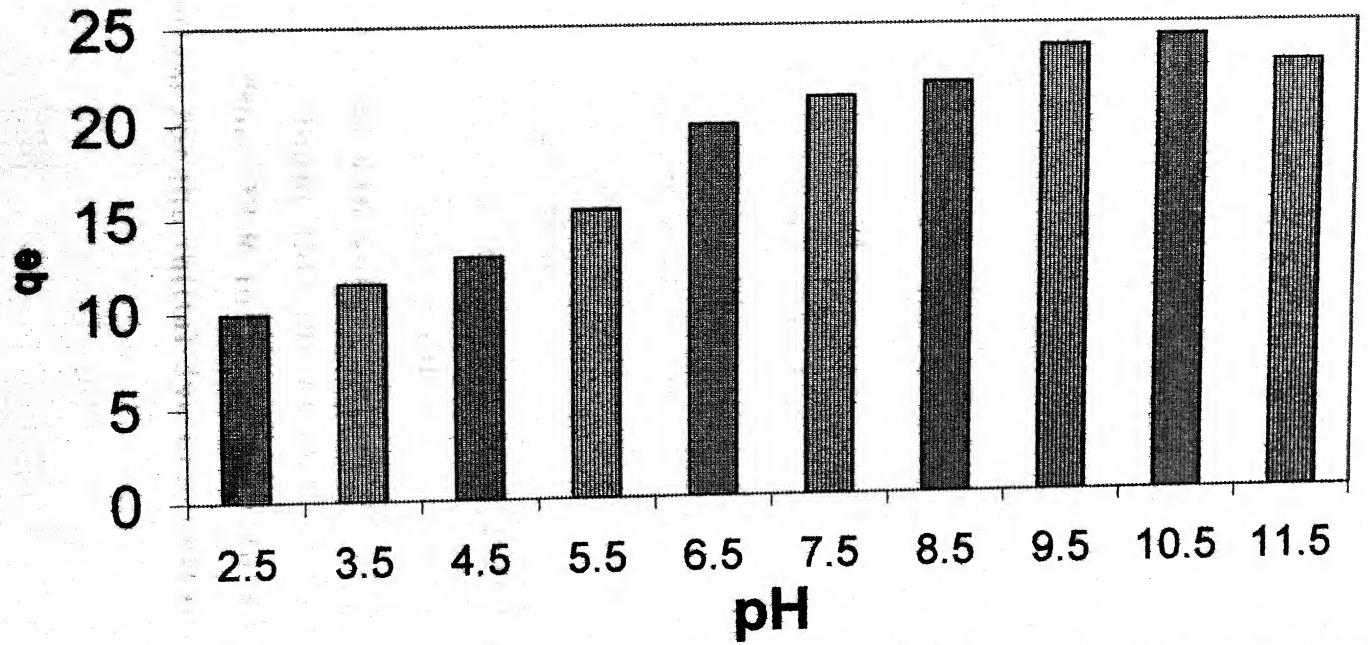


fig 7 Adsorption of Methylene Blue at different pH, Temperature 30 °C, Initial dye concentration 25 mg/l

SAFRANINE

Keeping the temperature at 30^{0}C and pH 7.5 in whole study, when the initial dye concentration was 25 mg/l the adsorption of Safranine on eucalyptus wood charcoal were found to be 88.40, 90.00,91.20, 92.80, 94.40, 95.20, 95.60, 96.00, 96.40, and 96.80 percent with the increasing contact time of 5,10,20,...90 min respectively and for initial dye concentration of 50 mg/l percent adsorption of dye were 85.00, 86.20, 87.60, 89.40, 90.60, 92.00, 92.40, 93.00, 93.40, 93.60 with the increasing contact time 5,10,20,....90 min. Similarly, for initial dye concentration of 75 mg/l the adsorption were found to be 82.66, 85.86, 86.80, 88.13, 89.33, 90.13, 91.20, 91.40, 91.60, and 91.73 percent with the increasing contact time of 5,10,20,....90 min respectively (table 12).

Effect of contact time: -

Fig 8 showed the effect of dye concentration on the extent of adsorption as a function of time for the initial dye concentration of 25,50, and 75 mg/l. It was found that the amount of dye adsorbed increased from 22.9 to 24.2, 42.5 to 46.8,62.0,to 68.8 mg/gm for the initial dye concentration of

Table 12. Kinetic study of Safranine on eucalyptus wood charcoal at different concentration and pH=7.5 and T=30°C .

s	time	initial concentration of dye		initial concentration of dye		initial concentration of dye	
no.	(min)	(25 mg/l)		(50 mg/l)		(75 mg/l)	
		amount adsorbed	% adsorption	amount adsorbed	% adsorption	amount adsorbed	% adsorption
		(mg/gms)		(mg/gms)		(mg/gms)	
1	5	22.1	88.4	42.5	85.0	62.0	82.7
2	10	22.5	90.0	43.1	86.2	64.4	85.9
3	20	22.8	91.2	43.8	87.6	65.1	80.8
4	30	23.2	92.8	44.7	89.4	66.1	88.1
5	40	23.6	94.4	45.3	90.6	67.0	89.3
6	50	23.8	95.2	46.0	92.0	67.6	90.1
7	60	23.9	95.6	46.2	92.4	68.4	91.2
8	70	24.0	96.0	46.5	93.0	68.6	91.4
9	80	24.1	96.4	46.7	93.4	68.7	91.6
10	90	24.2	96.8	46.8	93.6	68.8	91.7

25,50, and 75 mg/l respectively with the increase of contact time and achieved equilibrium in 90 min at temperature 30^0C and pH 7.5, afterwards no significant change was found. The time variation curves of adsorption were found to be smooth and continuous.

Adsorption dynamics:-

The straightline plot of log (qe-q) versus t for Safranine adsorption on eucalyptus wood charcoal at 30^0C (fig 9) indicated the applicability of Lagergren equation. The value of rate constant (K_{ad}) were $3.63x10^{-2}$, $3.55x10^{-2}$ and $3.56x10^{-2}$ min^{-1} for an initial concentration of 25,50 and 75 mg/l respectively at temperature of 30^0C and pH 7.5. The plot was linear for a wide range of concentrations and contact period.

The adsorption of Safranine dye on eucalyptus wood charcoal (particle size 180 mesh) at temperature 20^0C were 95.00, 92.00, 91.00, 90.00, 89.60, 88.00, 87.14, 84.75, 83.33, and 82.00 percent for increasing initial dye concentration $1x10^{-3}$to$1x10^{-2}$ mgl^{-1} (table 13a).The corresponding free energy (-ΔG) were 7.421, 6.772, 5.965, 5.704, 5.607, 5.252, 5.082,4.659,4.439, and 4.284, $kJmole^{-1}$ (table 14). At temperature of

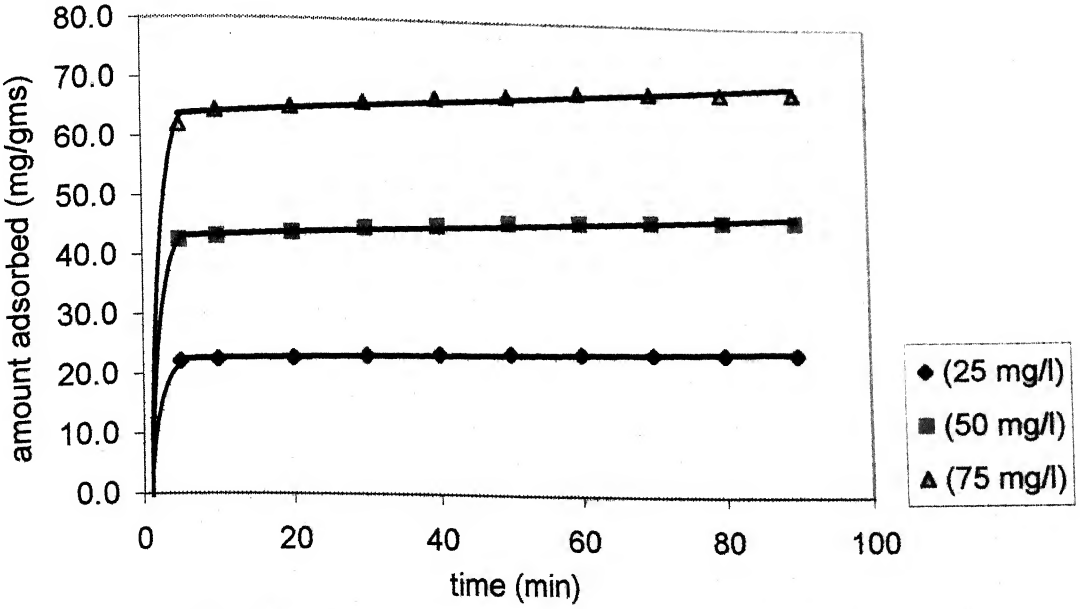


fig 8 Effect of concentration on adsorption of Safranine on eucalyptus wood charcoal at pH=7.5 and T=30°C

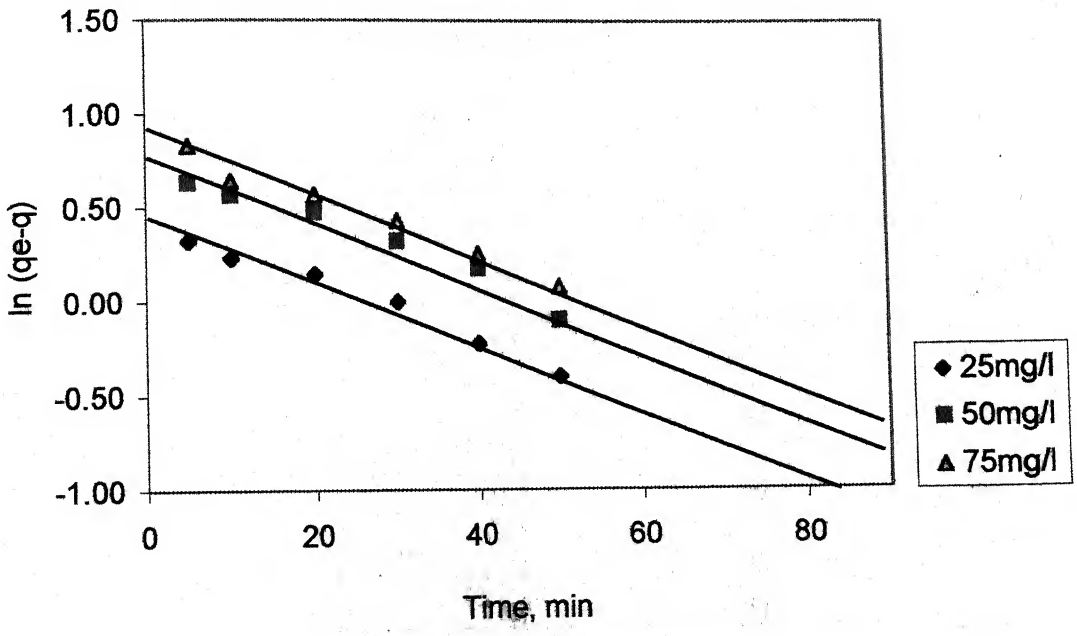


fig 9 Lagergren plot for Safranine

Table 13

Adsorption of Safranine dye on Eucalyptus wood charcoal (Particle size-180 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0. 2 gm)	% Adsorption
1	10	0.5	9.5	95.00
2	20	1.6	18.4	92.00
3	30	2.7	27.3	91.00
4	40	4.0	36.0	90.00
5	50	5.2	44.8	89.60
6	60	7.2	52.8	88.00
7	70	9.0	61.0	87.14
8	80	12.2	67.8	84.75
9	90	15.0	75.0	83.33
10	100	18.0	82.0	82.00

(a) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.8	9.2	92.00
2	20	2.5	17.5	87.50
3	30	3.8	26.2	87.33
4	40	5.2	34.8	87.00
5	50	6.5	43.5	87.00
6	60	8.8	51.2	85.33
7	70	10.5	59.5	85.00
8	80	13.5	66.5	83.12
9	90	15.9	74.1	82.33
10	100	18.9	81.1	81.10

30^0C the percent adsorption were 92.00, 87.50, 87.33, 87.00, 87.00, 85.33, 85.00, 83.12, 82.33, and 81.10 (table 13b). The corresponding values of free energy (-ΔG) were 6.467, 5.324, 5.290, 5.224, 5.224, 4.915, 4.857, 4.556, 4.438, and 4.226 $kJmole^{-1}$ (table 14). The respective values of enthalpy (-ΔH) were 35.86, 34.05, 26.07, 20.02, 17.02, 15.31, 11.76, 7.72, 4.44, 3.72 $kJmole^{-1}$ and that of entropy (-ΔS) were 95.43, 93.26, 67.46, 48.04, 38.29, 33.75, 22.40, 10.29, 3.35 and 1.89 $K^{-1}Jmole^{-1}$ (table 14). The values of K were 19.97, 15.37, 11.10, 9.99, 9.60, 8.32, 8.04, 6.55, 5.99, and 5.63 in the same order of increasing initial dye concentration (table 14).

For particle size (150 mesh) the adsorption of Safranine at temperature 20^0C were 93.10, 92.00, 91.66, 91.50, 89.60, 88.66, 88.28, 87.00, 84.33 and 81.40 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 15a). The corresponding values of free energy (-ΔG) was 6.623, 6.257, 6.156, 6.107, 5.423, 5.394, 5.312, 5.054, 4.592, 4.167 $kJmole^{-1}$ (table 16). At temperature of 30^0C, the percent adsorption was 90.00, 89.00, 88.66, 88.50, 87.00, 86.83, 86.42, 85.12, 82.77, and 80.60 for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table

Table 14

Thermodynamic Parameters for Safranine dye (Particle size – 180 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	7.421	6.467	35.86	95.43	19.97
2	6.772	5.324	34.05	93.26	15.37
3	5.965	5.290	26.07	67.46	11.10
4	5.704	5.224	20.02	48.04	09.99
5	5.607	5.224	17.02	38.29	09.60
6	5.252	4.915	15.31	33.75	08.32
7	5.082	4.857	11.76	22.40	08.04
8	4.659	4.556	07.72	10.29	06.55
9	4.439	4.438	04.44	03.35	05.99
10	4.284	4.266	03.72	01.89	05.63

Table 15

Adsorption of Safranine dye on Eucalyptus wood charcoal (Particle size 150 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.69	9.31	93.10
2	20	1.6	18.4	92.00
3	30	2.5	27.5	91.66
4	40	3.4	36.6	91.50
5	50	5.2	44.8	89.60
6	60	6.8	53.2	88.66
7	70	8.2	61.8	88.28
8	80	10.4	69.6	87.00
9	90	14.1	75.9	84.33
10	100	18.6	81.4	81.40

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	1.0	9.0	90.00
2	20	2.2	17.8	89.00
3	30	3.4	26.6	88.66
4	40	4.6	35.4	88.50
5	50	6.5	43.5	87.00
6	60	7.9	52.1	86.83
7	70	9.5	60.5	86.42
8	80	11.9	68.1	85.12
9	90	15.5	74.5	82.77
10	100	19.4	80.6	80.60

The corresponding free energy values were 5.896, 5.652, 5.575, 5.538, 5.224, 5.119, 5.114, 4.879, 4.504, 4.119 $kJmole^{-1}$ respectively (table 16). The respective values of enthalpy ($-\Delta H$) were 28.31, 24.30, 23.46, 23.06, 17.02, 11.44, 11.22, 10.28, 7.22, 3.21, $kJmole^{-1}$ and entropy ($-\Delta S$) values were 72.77, 60.54, 58.06, 56.88, 56.88, 38.91, 20.28, 19.82, 17.53, 8.81, 3.20 $K^{-1}Jmole^{-1}$ (table 16). The values of K were 14.47, 12.49, 11.99, 11.75, 8.92, 8.81, 8.53, 7.68, 6.37, and 5.37 in the same order of increasing initial dye concentration.

Effect of concentration: - Table 13a and 13b showed that the adsorption of Safranine decreased from 95.00 to 82.00% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 180 mesh) and at temperature 30^0C adsorption decreased from 92.00 to 81.10% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The curves at both temperatures showed decreased in adsorption with the increasing initial dye concentration (fig 10) . The curves at both temperatures were found to be smooth and continuous in nature.

Table 16

Thermodynamic Parameters for Safranine dye (Particle size – 150 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	6.623	5.896	28.31	72.77	14.47
2	6.257	5.652	24.30	60.54	12.49
3	6.156	5.575	23.46	58.06	11.99
4	6.107	5.538	23.06	56.88	11.75
5	5.423	5.224	17.02	38.91	08.92
6	5.394	5.119	11.44	20.28	08.81
7	5.312	5.114	11.22	19.82	08.53
8	5.054	4.879	10.28	17.53	07.68
9	4.592	4.504	07.22	08.81	06.37
10	4.167	4.119	03.21	03.20	05.37

(Table 15a and 15b) showed that the adsorption of Safranine decreased from 93.10 to 81.40 % by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 150 mesh) and at temperature 30^0C, adsorption decreased from 90.00 to 80.60 % by increasing dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The curves at both temperatures showed decreased in adsorption with the increasing dye concentration (fig 11) . The curves at both temperatures were found to be smooth and continuous.

Effect of particle size :- In table 15a and 13a results showed that the adsorption of Safranine increased from 81.40-93.10% to 83.33-95.00%. with decrease in particle size from 150-180 mesh at temperature 30^0C, results showed that the adsorption increased from 80.60-90.00 % to 81.10 to 92.00% with decreased in particle size from 150-180 mesh (table 15b, 13b). It was observed that adsorption increased with decrease in particle size.

Effect of Temperature: From table (13a and 13b) results indicated that the adsorption of Safranine decreased from 95.00-82.00 % to 92.00-

81.00% with increased in temperature from 20^{0}C to 30^{0}C for particle size 180 mesh . For particle size 150 mesh, results indicated that the percent adsorption of Safranine decreased from 93.10-81.40% to 90.50-86.60% with increasing temperature 20^{0}C to 30^{0}C (Table 15a and 15b) it was observed that adsorption decreased with increase of temperature.

It was found that the free energy (-ΔG) decreased from 5.938-4.037 to 5.429-3.996 kJmole^{-1} with the increase in of temperature 20^0 C to 30^{0}C for particle size 180 mesh(table 14), and for particle size 150 mesh free energy (-ΔG) decreased from 5.054-3.535 to 4.692-3.539 kJmole^{-1} with the rise of temperature from 20° C to 30^{0}C (table 16). The values of entropy (-ΔS) and enthalpy (-ΔH) changes were found to be negative (table 14, 16).

Adsorption Isotherms: -

The results favoured the adsorption of Safranine on eucalyptus wood charcoal at different temperatures obeyed Freundlich adsorption isotherm. The data were fitted to the linear form of Freundlich equation

$$\ln qe = \ln K_f + (1/n) \ln Ce$$

The plot (fig 12, 13) of ln qe versus ln Ce for various initial concentration was found to be linear indicating the applicability of Freundlich adsorption isotherm for particle size 180 mesh at 20^0C the values of K_f and 1/n was 2.66,0.638 respectively. Similarly, at 30^0C the value of K_f and 1/n was 2.30 and 0.719 respectively. the value of K_f and 1/n for particle size 150 mesh at 20°C was 2.62 and 0.663 respectively. Similarly,at 30°C the values of K_f and 1/n was 2.23 and 0.789 respectively. It was found that the value of K_f decreased with the rise of temperature showing that the rate of adsorption also decreased with rise of temperature.

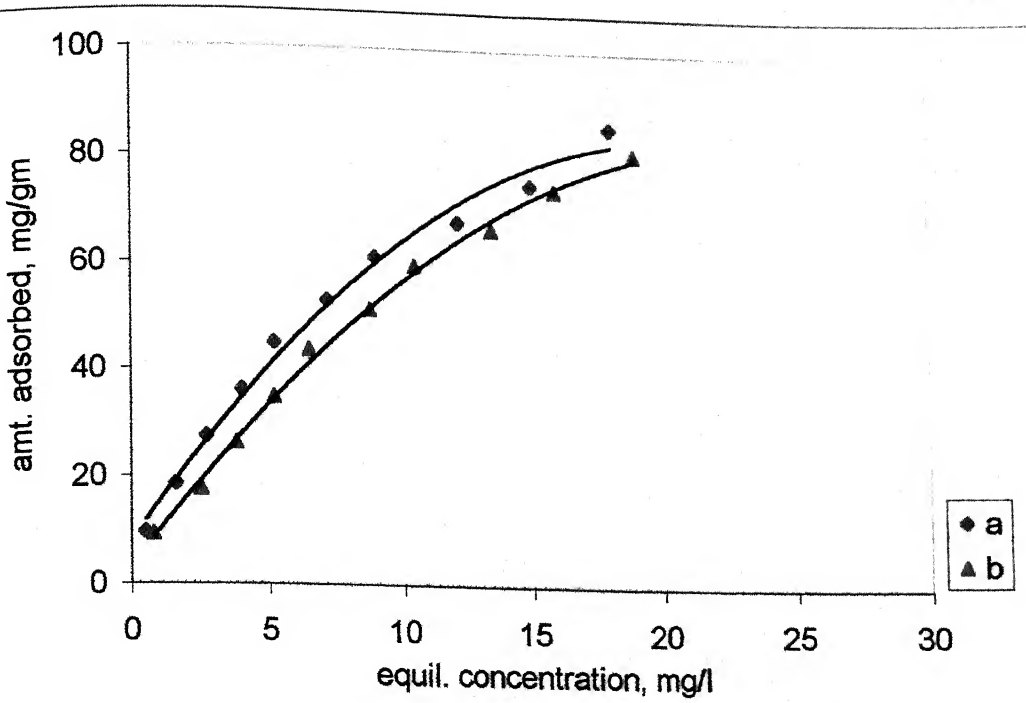


fig 10 Equilibrium isotherm of Safranine
(Particle Size 180 Mesh) a - 20°C, b - 30°C

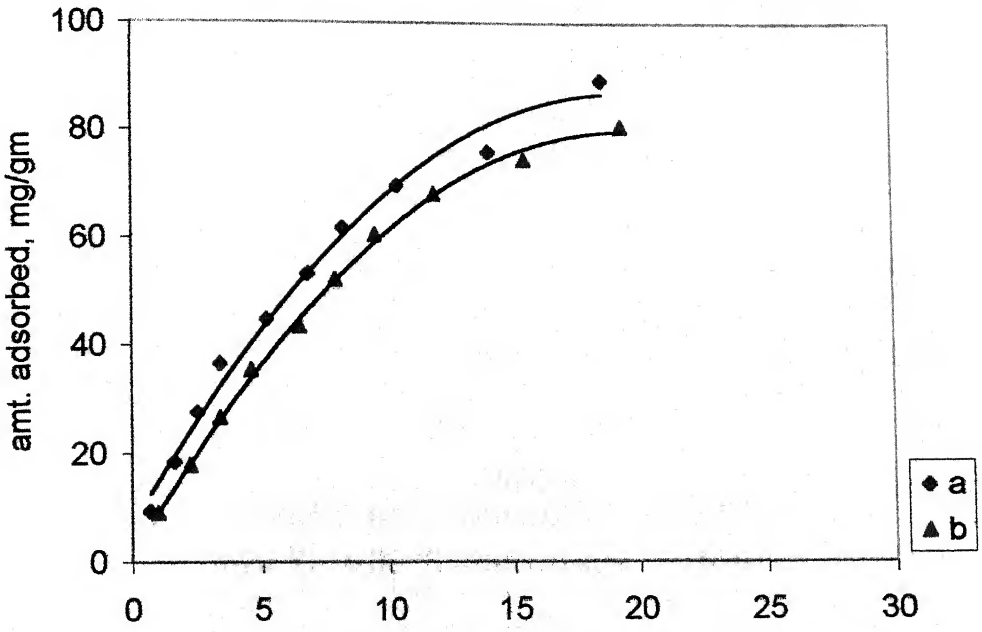


fig 11 equilibrium isotherm of Safranine
(Particle Size 150 Mesh), a - 20°C, b - 30°C

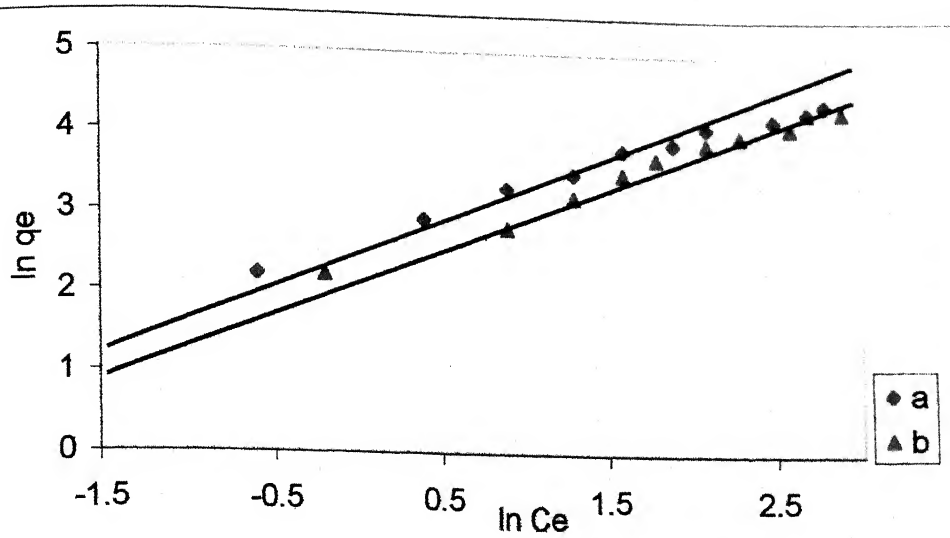


Fig 12 Freundlich adsorption isotherm of Safranine
a-20 °C b-30 °C (Particle size 180 Mesh)

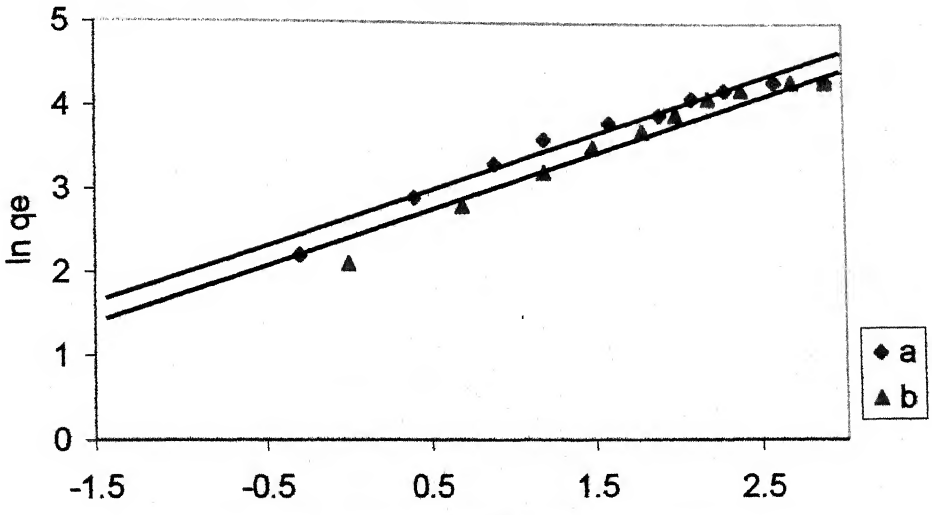


Fig 13 Freundlich adsorption isotherm of Safranine
a-20 °C b-30 °C (Particle size 150 Mesh)

Effect of pH: - The effects of pH on the adsorption of Safranine dye showed in fig 14. The percent adsorption of safranine dye were 31.60, 43.20, 50.00, 59.60, 66.40, 76.80, 80.40, 86.80, 91.60, and 87.20 with increasing pH values from 2.5 to 11.5 at temperature 30^0C and concentration 25 mg/l (table17). It observed that with the increased of pH from 2.5 to 10.5, adsorption of Safranine dye increase from 31.60 to 91.60% by eucalyptus wood charcoal and above the pH of 10.5 adsorption was found to decreased gradually.

Table 17
Adsorption of Safranine at different pH, Temperature 30 °C, Initial dye concentration 25 mg/l

S no	pH	Equilibrium dye concentration (mg/l)	Amount of dye adsorbed (mg/gm)	% adsorption
1	2.5	17.1	17.9	31.60
2	3.5	14.2	10.8	43.20
3	4.5	12.5	12.5	50.00
4	5.5	10.1	14.9	59.60
5	6.5	8.4	16.4	66.40
6	7.5	5.8	19.2	76.80
7	8.5	4.9	20.1	80.40
8	9.5	3.3	21.7	86.80
9	10.5	2.1	22.9	91.60
10	11.5	3.2	21.8	87.20

Table 18

Freundlich Constant for Safranine

Particle size	Temperature	K_f	1/n
180 Mesh	20^0 C	2.66	0.638
	30^0 C	2.30	0.719
150 Mesh	20^0 C	2.62	0.663
	30^0 C	2.23	0.789

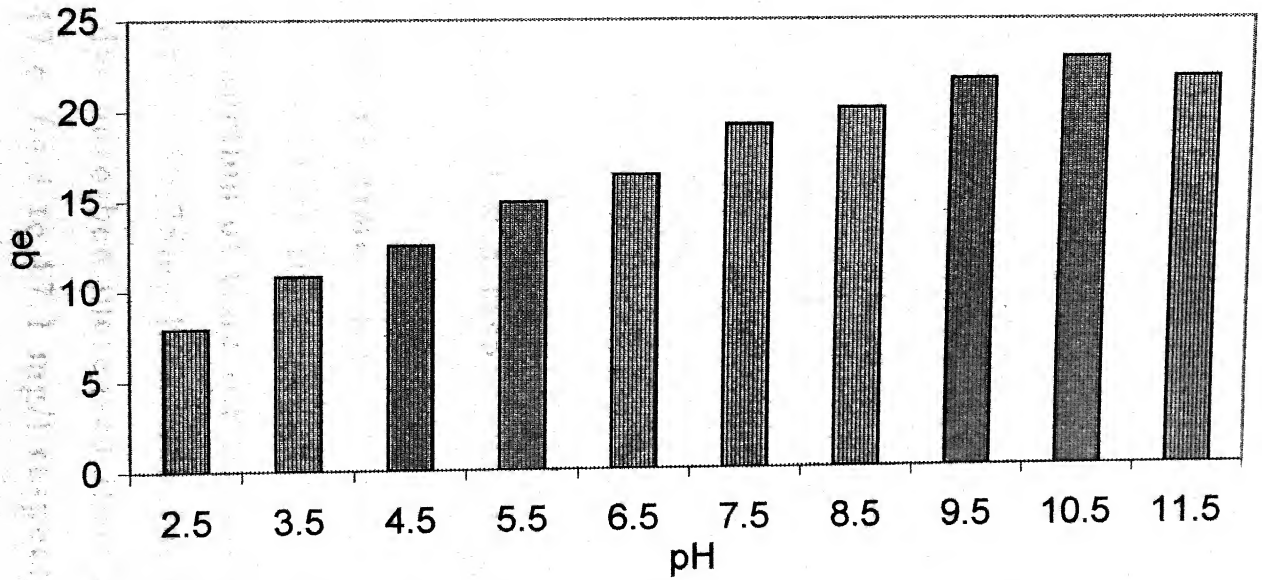


fig 14 Adsorption of Safranine at different pH, Temperature 30 °C, Initial dye Concentration 25 mg/l

CRYSTAL VIOLET

The adsorption of Crystal Violet on eucalyptus wood charcoal were found to be 91.60, 92.00, 94.00, 95.60, 96.00, 97.60, 98.40, 98.80, 99.20,and 100.00 percent for the initial dye concentration 25 mg/l with the increasing contact time 5,10,20,....., 90 min and for initial dye concentration 50mg/l the percentage adsorption were 88.00, 89.00, 90.21, 91.80, 92.20, 93.80, 94.40, 94.40, 95.00, and 95.20 with the increasing contact time 5,10,20,....., 90 min at temperature 30^0C and pH 7.5 respectively. Similarly, for initial dye concentration 75 mg/l the adsorption were found to be 85.46, 86.93, 88.53, 89.46, 90.50, 91.73, 92.13, 92.93, 93.33, and 93.46 with the increasing contact time5,10,20,....., 90 min respectively(table 19)

.

Effect of contact time –Fig 15 showed the effects of the concentration on the extent of adsorption as a function of time for the initial dye concentration of 25,50,75mg/l. It was found that the amount of dye adsorbed increased from 22.9 to 24.9, 44.0 to 47.6, 64.1 to 17.1 mg/l respectively

Table 19 Kinetic study of Crystal violet on eucalyptus wood charcoal at different concentration and pH=7.5 and T=30°C

s	time	initial concentration of dye		initial concentration of dye		initial concentration of dye	
no.	(min)	(25 mg/l)		(50 mg/l)		(75 mg/l)	
		amount adsorbed	% adsorption	amount adsorbed	% adsorption	amount adsorbed	% adsorption
		(mg/gms)		(mg/gms)		(mg/gms)	
1	5	22.9	91.6	44.0	88.0	64.1	85.5
2	10	23.0	92.0	44.5	89.0	65.2	86.9
3	20	23.5	94.0	45.1	90.2	66.4	88.5
4	30	23.9	95.6	45.9	91.8	67.1	89.5
5	40	24.0	96.0	46.1	92.2	67.9	90.5
6	50	24.4	97.6	46.9	93.8	68.8	91.7
7	60	24.6	98.4	47.2	94.4	69.1	92.1
8	70	24.7	98.8	47.4	94.8	69.7	92.9
9	80	24.8	99.2	47.5	95.0	70.0	93.3
10	90	25.0	100.0	47.6	95.2	70.1	93.5

with the increase of time and achieved equilibrium in 90 min at temperature 30^0C and pH 7.5,however, afterwards no significant change was found. The time variation curves of adsorption were found to be smooth and continuous.

Adsorption dynamics :- The straight line plot of log (qe-q) versus t for Crystal Violet adsorption by eucalyptus wood charcoal at 30^0C (fig 30) indicated the applicability of Lagergren equation. The values of rate constant (K_{ad}) was $2.94x10^{-2}$, $3.32x10^{-2}$, $3.15x10^{-2}$ min^{-1} for an initial concentration of 25,50 and 75 mg/l respectively at temperature 30^0C and pH 7.5. The plot was linear for a wide range of concentrations and contact period.

The adsorption of Crystal Violet on eucalyptus wood charcoal (particle size 180 mesh) at temperature 20^0C were 98.00, 96.50, 95.66, 94.50, 93.60, 92.33, 91.42, 91.00, 90.00, and 89.50 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}(table 20a). The corresponding values of free energy ($-\Delta G$) were 9.692, 8.305, 7.776, 7.185, 6.810, 6.362, 6.086, 5.965,95.704, and 5.583 $kJmole^{-1}$ (table 21). At temperature 30^0C the percent adsorption of

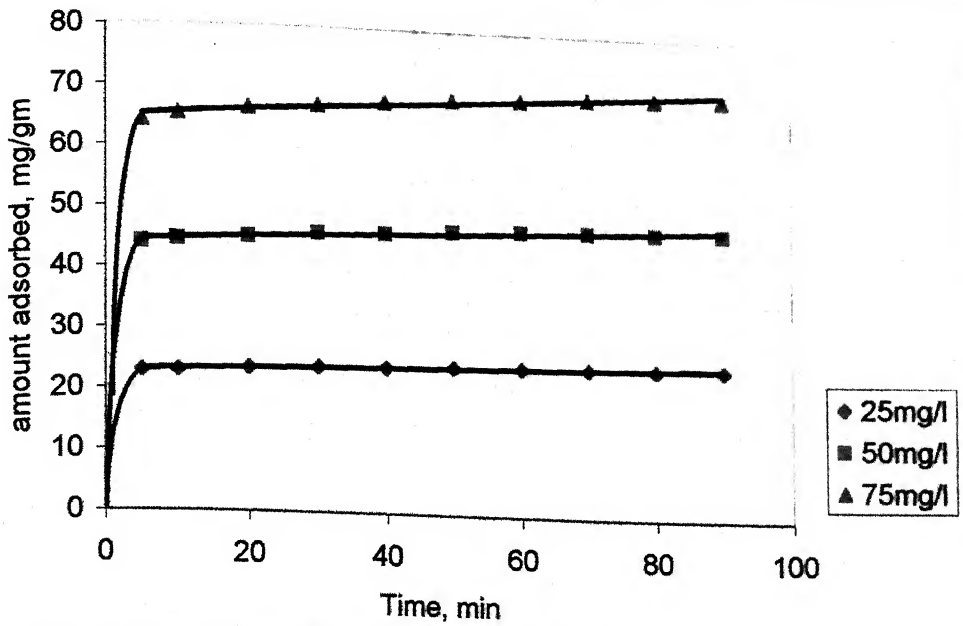


fig 15 Effect of concentration and time on adsorption of Crystal violet on eucalyptus wood charcoal at pH=7.5 and T=30oC

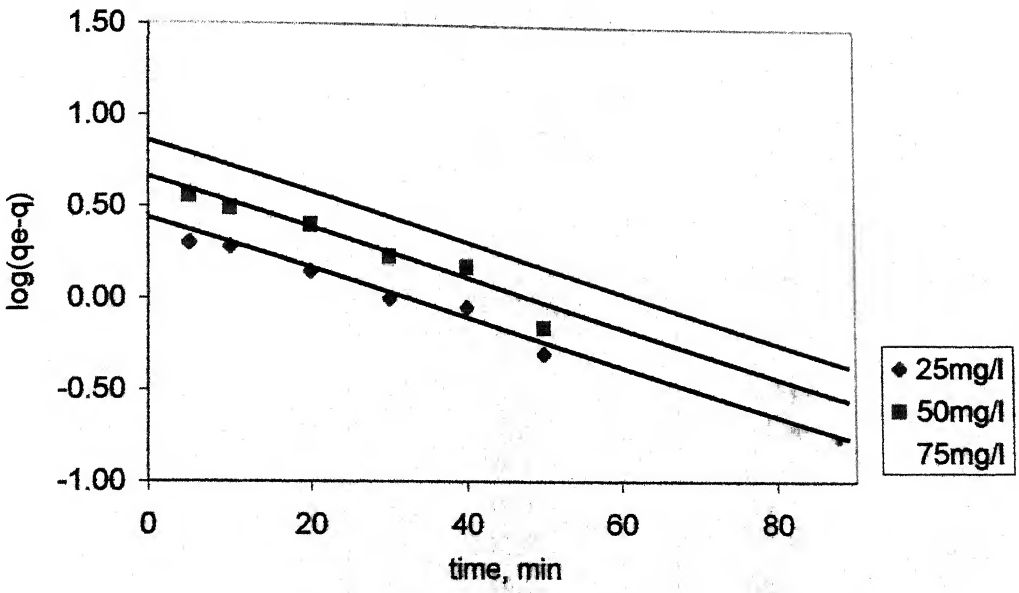


Fig 16 Lagergren plot for Crystal violet

Table 20

Adsorption of Crystal Violet dye on Eucalyptus wood charcoal (Particle size 180 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.2	9.8	98.00
2	20	0.7	19.3	96.50
3	30	1.3	28.7	95.66
4	40	2.2	37.8	94.50
5	50	3.2	46.8	93.60
6	60	4.6	55.4	92.33
7	70	6.0	64.0	91.42
8	80	7.2	72.8	91.00
9	90	9.0	81.0	90.00
10	100	10.5	89.50	89.50

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium of dye concentration ($1x10^{-4}$ mg/l)	Amount of dyes adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.4	9.60	96.00
2	20	1.4	18.6	93.00
3	30	2.4	27.6	92.00
4	40	3.9	36.1	90.25
5	50	5.5	44.5	89.00
6	60	7.2	52.8	88.00
7	70	9.2	60.8	86.85
8	80	10.8	69.2	86.50
9	90	12.2	77.8	86.44
10	100	14.0	86.0	86.00

Crystal violet were 96.00, 93.00, 92.00, 90.25, 89.00, 88.00, 86.85, 86.50,86.44, and 86.00 for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 20b). The corresponding values of free energy ($-\Delta G$) were 8.242, 6.809, 6.467, 5.961, 5.652, 5.429, 5.196, 5.127,5.117, and 5.034 kJ $mole^{-1}$ (table 21).

The respective values of enthalpy ($-\Delta H$) were 52.89, 52.89, 46.78, 43.68, 41.32, 34.18, 32.61, 30.94, 23.21, and 21.95 $kJmole^{-1}$ and entropy values ($-\Delta S$) were 144.95, 144.95.130.88, 122.46,115.80, 93.34, 89.00, 83.80, 58.74, and 54.92 $K^{-1}Jmole^{-1}$ (table 21). The values of K were 49.95, 49.95, 23.05, 18.16, 15.61, 13.03, 11.65, 11.10, 9.99, and 9.51 in the same order of increasing initial dye concentration (table 21).

For particle size 150 mesh, the adsorption of Crystal violet at temperature 20^0C were 97.20, 95.25, 94.00, 92.50, 90.80, 89.33, 88.71, 87.12, 84.44, and 82.10 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 22a). The corresponding values of free energy ($-\Delta G$) were 8.858, 7.549, 6.970, 6.417, 5.911, 5.544, 5.404, 5.078, 4.610, and 4.262 $kJmole^{-1}$ (table 23). At temperature 30^0C, the adsorption

Table 21

Thermodynamic Parameters for adsorption of Crystal Violet(particle size 180 mesh)

Sr. No	-Δ G (kJ Mol^{-1})		- Δ H (kJ Mol^{-1})	- Δ S ($K^{-1}Jmol^{-1}$)	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	9.692	8.242	52.89	144.95	49.95
2	8.305	6.809	52.89	144.95	49.95
3	7.776	6.467	46.78	130.88	23.05
4	7.185	5.961	43.68	122.46	18.16
5	6.810	5.652	41.32	115.80	15.61
6	6.362	5.429	34.18	93.34	13.03
7	6.086	5.196	32.61	89.00	11.65
8	5.965	5.127	30.94	83.80	11.10
9	5.704	5.117	23.21	58.74	9.99
10	5.583	5.034	21.95	54.92	9.516

Table 22

Adsorption of Crystal Violet dye on Eucalyptus wood charcoal (Particle size 150 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.28	9.72	97.20
2	20	0.95	19.05	95.25
3	30	1.8	28.2	94.00
4	40	3.0	37.0	92.50
5	50	4.6	45.4	90.80
6	60	6.4	53.6	89.33
7	70	7.9	62.1	88.71
8	80	10.3	69.7	87.12
9	90	14.0	76.0	84.44
10	100	17.9	82.1	82.10

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.44	9.56	95.60
2	20	1.4	18.6	93.00
3	30	2.6	27.4	91.33
4	40	4.1	35.9	89.75
5	50	6.0	44.0	88.00
6	60	7.9	52.1	86.83
7	70	9.5	60.5	86.42
8	80	11.9	68.1	85.12
9	90	15.9	74.1	82.33
10	100	19.7	80.3	80.30

w ere 95.62, 93.00, 91.33, 89.75, 88.00, 86.83, 86.42, 85.12, 82.33 and 80.30 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 22b). The corresponding values of free energy ($-\Delta G$) were 7.998, 6.809, 6.262, 5.833, 5.429, 5.191, 5.114, 4.876, 4.438,and 4.160 $kJmole^{-1}$(table 23).

The respective values of enthalpy ($-\Delta H$) were 34.49, 29.59, 28.06, 23.83, 20.27, 16.06, 14.07, 11.01, 9.71, and 7.31 $kJmole^{-1}$ and entropy ($-\Delta S$) values were 86.01, 73.96, 70.77, 58.45, 48.20, 35.31, 29.08, 19.93, 17.11, and 11.53 K^{-1} $Jmole^{-1}$ (table 23). The values of K were 35.68, 21.03, 16.65, 13.32, 10.86, 9.36, 8.85, 7.76, 6.42, 5.58 in the same order of increasing initial dye concentration (table 23)

Effect of concentration :- Table 20(a) and 20(b) showed that the adsorption of Crystal violet decreased from 98.00 to 89.50% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0c (particle size – 180 mesh) and at temperature 30^0c, adsorption decreased from 96.00 to 86.00% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$

Table 23

Thermodynamic Parameters of Crystal Violet dye (Particle size – 150 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	8.858	7.998	34.49	86.01	35.68
2	7.549	6.809	29.59	73.96	21.03
3	6.970	6.262	28.06	70.77	16.65
4	6.417	5.833	23.83	58.45	13.32
5	5.911	5.429	20.27	48.20	10.86
6	5.544	5.191	16.06	35.31	09.36
7	5.404	5.114	14.07	29.08	08.85
8	5.078	4.876	11.01	19.93	07.76
9	4.610	4.438	09.71	17.11	06.42
10	4.262	4.160	07.31	11.53	05.58

mgl^{-1}. The nature of curves at both temperatures showed an increased in amount of dye adsorbed on increase in dye concentration (fig17). The both curves were found to be smooth and continuous in nature.

The results showed (table 22(a) & (b)) that adsorption of Crystal violet decreased from 97.20, to 82.10% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 150 mesh) and at 30^0C, adsorption decreased from 95.60 to 80.30 % by increasing initial dye concentration $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The nature of curves at both temperatures showed an increased in amount of dye adsorbed on increase in dye concentration (fig18). The both curves were found to be smooth and continuous in nature.

Effect of particle size :- The results showed (table 22(a) &20(a)) that the adsorption of Crystal violet increased from 82.10-97.20 to 89.50-98.00% with decrease in particle size from 150-180 mesh at temperature 20^0C. At temperature 30^0C, results showed (table 22(b) and 20(b)) that adsorption increased from 80.30-95.60 % to

86.00-96.00 % with decrease in particle size from 150-180 mesh. It was observed that adsorption increased with decreases in particle size.

Effect of temperature: - The results indicated (table 20(a) and 20(b)) that the adsorption of Crystal violet decreased from 98.00-89.50 to 96.00-86.00% with increase in temperature from 20^0C to 30^0C for particle size 180 mesh. For particle size 150 mesh, results (table 22(a) and 22(b)) indicated that percent adsorption of Crystal violet decreased from 97.20-82.10 % to 95.60-80.30 % with increasing temperature 20^0C to 30^0C. It was observed that adsorption decreased with the rise of temperature. It was found that the free energy ($-\Delta G$) decreased from 9.692-5.583 to 8.242-5.034 $kJmole^{-1}$ (table 21) on increase in temperature from 20 to 30^0C for particle size 180 mesh. And for particle size 150, free energy ($-\Delta G$) decreased from 8.858-4.262 to 7.998-4.160 $kJmole^{-1}$ with the increasing temperature 20°C to 30^0C (table). The values of entropy ($-\Delta S$) and enthalpy ($-\Delta H$) change were found to be negative (table 21 and 23).

Adsorption Isotherms: - The results favoured that the adsorption of Crystal violet on eucalyptus

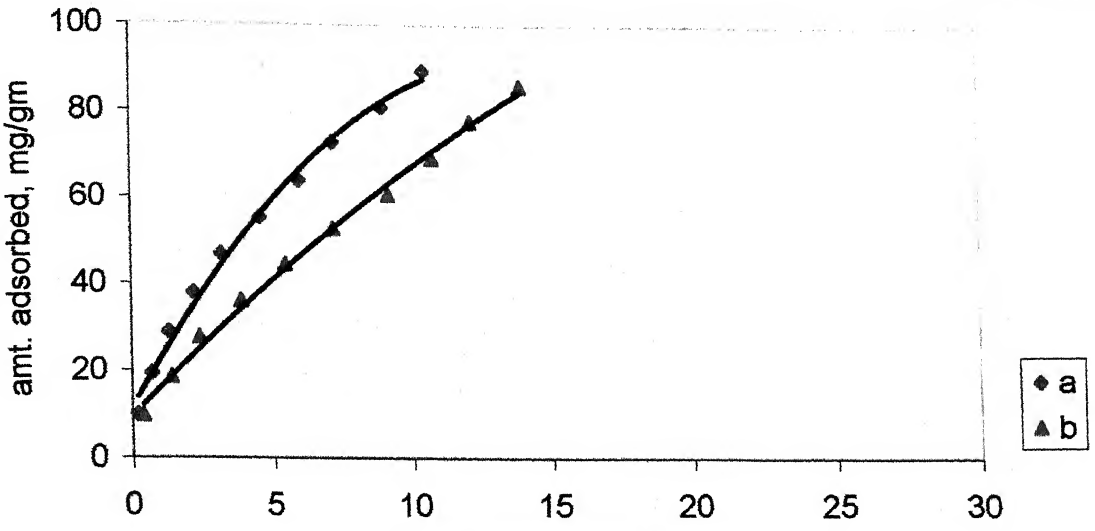


fig 17 Equilibrium isotherm of Crystal Violet
(Particle size180 mesh) a - 20°C, b - 30°C

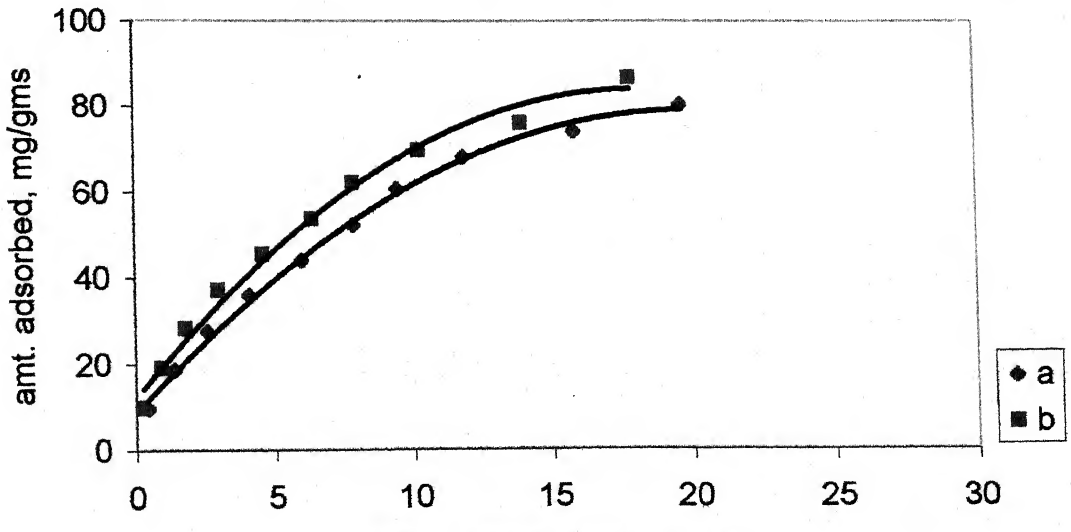


fig 18 equilibrium isotherm of Crystal Violet
(particle size 150 mesh) a - 20°C, b - 30°C

wood charcoal at different temperatures obeyed Freundlich adsorption isotherm. The data were fitted to the linear form of Freundlich equation

$$\ln qe = \ln K_f + (1/n) \ln Ce$$

The plot of ln qe versus ln Ce for various initial concentrations was found to be linear indicating the applicability of Freundlich adsorption isotherm. For particle size 180 mesh at 20^0C the values of K_f and 1/n was 3.13, 0.568 respectively. Similarly, at 30^0C ,the values of K_f and 1/n was 2.73 and 0.621respectively. For particle size 150 the values of K_f and 1/n at 20^0C was 2.99 and 0.520 respectively. Similarly, at 30^0Cthe values of K_f and 1/n was 2.75 and 0.551 respectively. It was clear from (table 25) that value of K_f decreased with the rise of temperature showing that the rate of adsorption decreased with the rise of temperature.

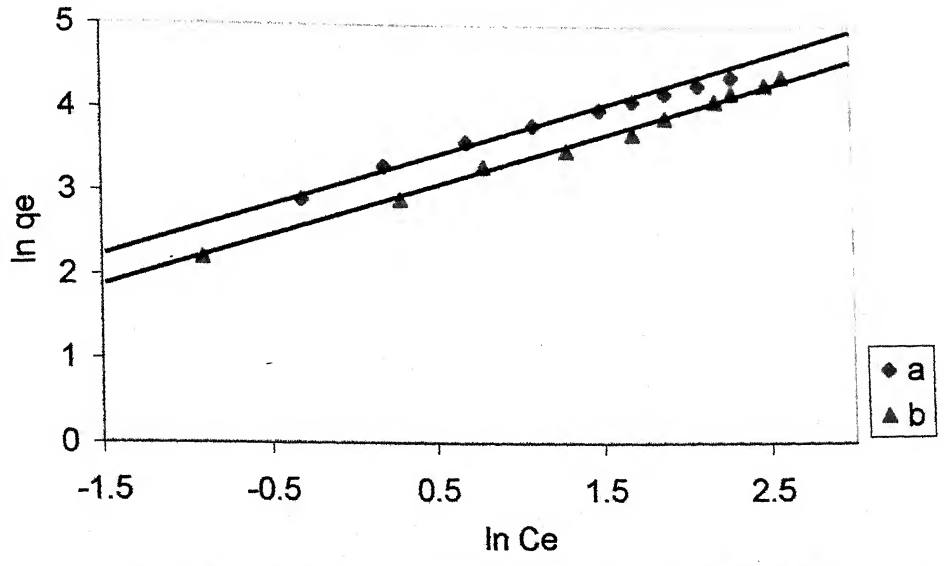


Fig 19 Freundlich adsorption isotherm of Crystal Violet
a-20 °C b-30 °C (Particle size 180 Mesh)

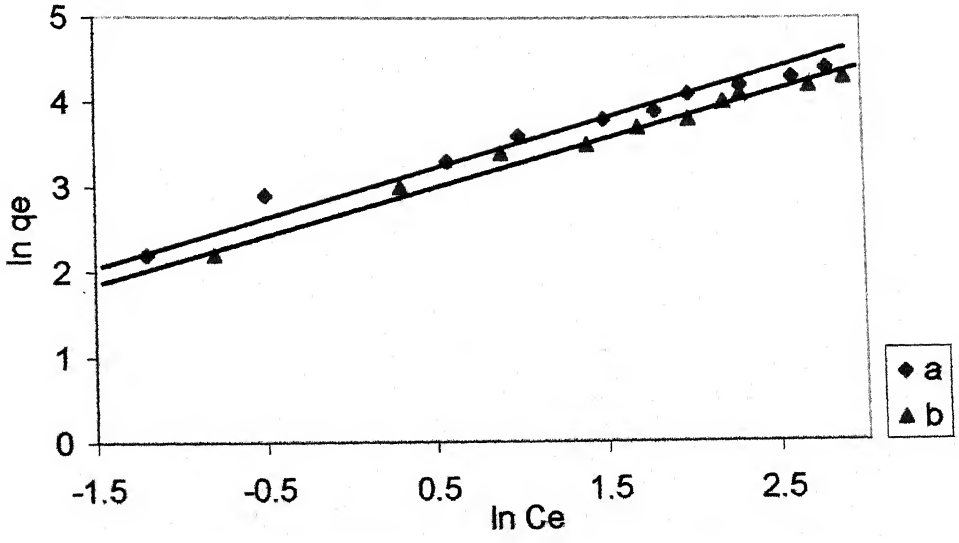


Fig 20 Freundlich adsorption isotherm of Crystal Violet
a-20 °C b-30 °C (Particle size 150 mesh)

Effect of pH: - The effects of pH on the adsorption of Crystal violet dye showed in fig 21. The percent adsorption of Crystal violet were 34.40, 47.60, 54.00, 60.40, 70.00, 77.20, 82.80, 86.00, 94.00 and 88.40 with the increasing pH values from 2.5 to 11.5 at temperature 30^0C and concentration 25 mg/l (table24) It was observed that with increased of pH from 2.5 to 10.5 the adsorption of Crystal violet dye increase from 34.40 to 94.00% by eucalyptus wood charcoal and above this pH adsorption was found to decreased gradually up to pH of 10.5.

Table 24

Adsorption of Crystal Violet dye at Different pH, Temperature 30 °C, Initial dye concentration 25 mg/l

S No	pH	Equilibrium dye concentration (mg/l)	Amount of dye adsorbed (mg/gm)	% adsorption
1	2.5	16.4	8.6	34.40
2	3.5	13.1	11.9	47.60
3	4.5	11.5	13.5	54.00
4	5.5	9.9	15.1	60.40
5	6.5	7.5	17.5	70.00
6	7.5	5.7	19.3	77.20
7	8.5	4.3	20.7	82.20
8	9.5	3.5	21.5	86.00
9	10.5	1.5	23.5	94.00
10	11.5	2.9	22.1	88.40

Table 25

Freundlich Constant for Crystal Violet

Particle Size	Temperature	K_f	1/n
180 Mesh	20^0 C	3.13	0.568
	30^0 C	2.73	0.621
150 Mesh	20^0 C	2.99	0.520
	30^0 C	2.75	0.551

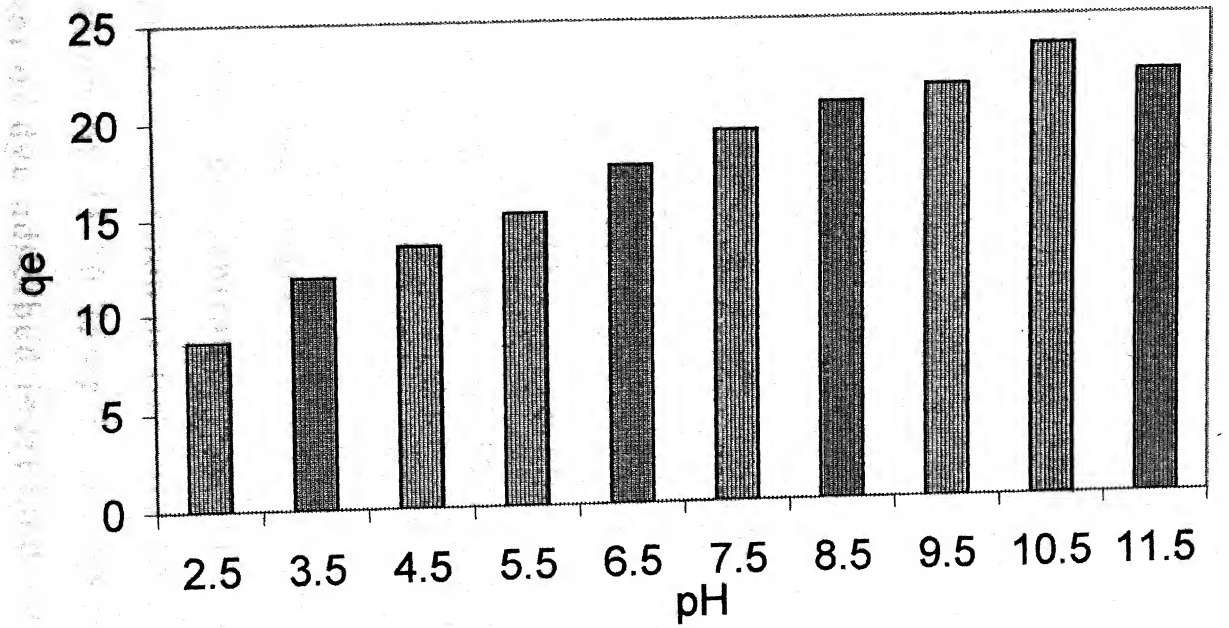


fig 21 Adsorption of Crystal Violet at different pH, Temperature 30 °C, Initial dye concentration 25 mg/l

Malachite green

When the initial dye concentration was 25 mg/l the adsorption of Malachite green on eucalyptus wood charcoal was found to be 86.00, 87.60, 88.00, 89.20, 90.40, 90.80, 91.60, 92.00, 93.20, and 94.60 with the increasing contact time 5,10,20,.....90 min respectively and for initial dye concentration of 50mg/l the percent adsorption of dye was 82.40, 83.80, 84.40, 85.60, 86.20, 87.80, 88.20, 89.00, 91.40, and 92.60 with the increasing contact time for 5,10,20,....., 90 min respectively at temperature 30^0C and pH 7.5. Similarly, for initial dye concentration of 75 mg/l the adsorption was found to be 79.86, 80.66, 81.86, 83.46, 84.53, 85.46, 87.60, 88.13, 89.06, and 90.40 percent with the increasing time 5,10,20,....90 min respectively(table 26).

Effect of contact time :- Fig 22 showed the effect of dye concentration on the extent of adsorption as a function of time for the initial dye concentration of 25,50,75mg/l. It was found that the amount of dye adsorbed increased from 21.5 to 23.9, 41.2 to 46.3, 59.9 to 67.8 mg/gm for the

Table 26. Kinetic study of Malachite green on eucalyptus wood charcoal at different concentration and pH=7.5 and T=30°C

s	time	initial concentration of dye		initial concentration of dye		initial concentration of dye	
no.	(min)	(25 mg/l)		(50 mg/l)		(75 mg/l)	
		amount adsorbed	% adsorption	amount adsorbed	% adsorption	amount adsorbed	% adsorption
		(mg/gms)		(mg/gms)		(mg/gms)	
1	5	21.5	86.0	41.2	82.4	59.9	79.9
2	10	21.9	87.6	41.9	83.3	60.5	80.6
3	20	22.0	88.0	42.2	84.4	61.4	81.9
4	30	22.3	89.2	42.8	85.6	62.6	83.5
5	40	22.6	90.4	43.1	86.2	63.4	84.5
6	50	22.7	90.8	43.9	87.8	64.1	85.5
7	60	22.9	91.6	44.1	88.2	65.7	87.6
8	70	23.0	92.0	44.5	89.0	66.1	88.1
9	80	23.3	93.2	45.7	91.4	66.8	89.1
10	90	23.9	94.6	46.3	92.0	67.8	90.4

initial dye concentration of 25,50, and 75 mg/l respectively with the increased of contact time and achieved equilibrium in 90 min at temperature 30^0Cand pH7.5 and afterwards no significant change was found. The time variation curves of adsorption were found to be smooth and continuous

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Adsorption dynamics :- The straight line plot of log (qe-q) versus t for Malachite green adsorption by eucalyptus wood charcoal at 30°C (fig 23) indicated the applicability of Lagergren equation. The values of rate constant were $1.64x10^{-2}$,$2.23x10^{-2}$, and $2.64x10^{-2}$ min^{-1} at initial concentration of 25,50, and 75 mg/l respectively at temperature of 30^0C.

The adsorption of Malachite Green on eucalyptus wood charcoal (particle size 180mesh) at temperature 20^0C were 94.00, 93.50, 91.00, 90.25, 87.60, 87.00, 85.85, 83.87, 82.55, and 81.00 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}(table27a).

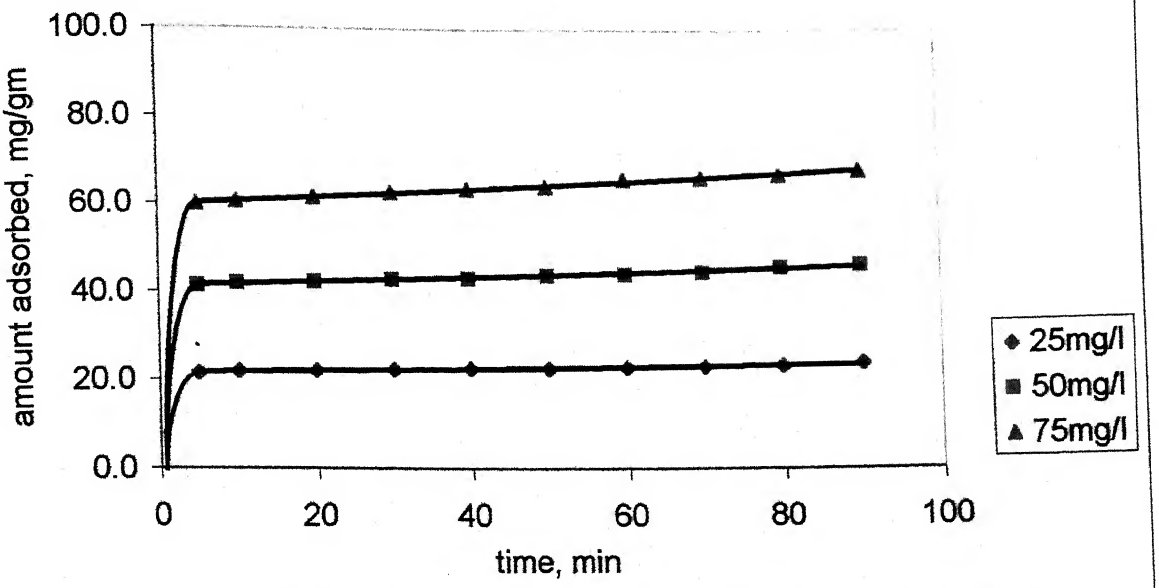


fig 22 Effect of concentration and time on adsorption of Malachite green on eucalyptus charcoal at pH=7.5 and T=30°C

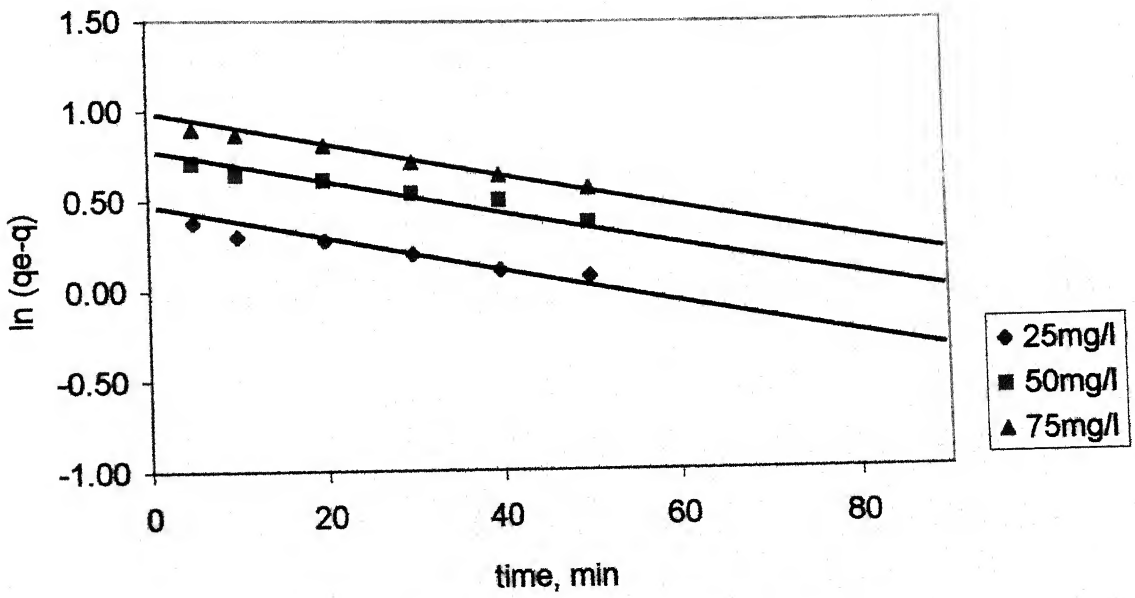


fig 23 Lagergren plot for Malachite green

Table 27

Adsorption of Malachite green dye on Eucalyptus wood charcoal (Particle size 180 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/L)	Equilibrium dye concentration ($1x10^{-4}$ mg/L)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.6	9.5	94.00
2	20	1.3	18.7	93.50
3	30	2.7	27.3	91.00
4	40	3.9	36.1	90.25
5	50	6.2	43.8	87.60
6	60	7.8	52.2	87.00
7	70	9.9	60.1	85.85
8	80	12.9	67.1	83.87
9	90	15.7	74.3	82.55
10	100	19.0	81.0	81.00

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.9	09.1	91.00
2	20	1.9	18.1	90.50
3	30	3.9	26.1	87.00
4	40	5.4	34.6	86.50
5	50	8.0	42.0	84.00
6	60	10.0	50.0	83.33
7	70	11.9	58.1	83.00
8	80	14.1	65.9	82.37
9	90	17.0	73.0	81.11
10	100	20.5	79.5	79.50

The corresponding values of free energy were 6.920, 6.257, 5.965, 5.767, 5.171, 5.054, 4.845, 4.520, 4.326, and 4.114 $kJmole^{-1}$(table 28). At temperature 30^0C the percent adsorption were 91.00, 90.50, 87.00, 86.50, 84.00, 83.33, 83.00, 82.37, 81.11, and 79.50 for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}(table 27b). The corresponding values of free energy ($-\Delta G$) were 6.166, 5.652, 5.224, 5.127, 4.692, 4.588, 4.537, 4.445, 4.267, and 4.058 kJ $mole^{-1}$ (table 28)

The respective values of enthalpy ($-\Delta H$) were 30.94, 28.95, 28.06, 24.83, 19.42, 18.95, 14.04, 6.78, 6.07 and 5.79, k J $mole^{-1}$ and entropy ($-\Delta S$) values were 80.43, 74.44, 74.14, 63.96, 47.81, 46.63, 30.85, 7.58, 5.85, and 5.62 $K^{-1}Jmole^{-1}$(table 28) The values of K were 16.32, 12.49, 11.10, 10.24, 8.05, 7.68, 7.06, 6.19, 5.73, and 5.26 in the same order of increasing initial dye concentration (table 28).

For particle size 150 mesh, the adsorption of Malachite green at temperature 20^0C were 92.50, 91.00, 90.00, 89.75, 89.20, 88.16, 87.71, 84.87, 82.11, and 79.20 for increasing

Table 28

Thermodynamic Parameters of Malachite green dye (Particle size – 180 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	6.920	6.166	30.94	80.43	16.32
2	6.257	5.652	28.95	74.44	12.49
3	5.965	5.224	28.06	74.14	11.10
4	5.767	5.127	24.83	63.96	10.24
5	5.171	4.692	19.42	47.81	08.05
6	5.054	4.588	18.95	46.63	07.68
7	4.845	4.537	14.04	30.85	07.06
8	4.520	4.445	06.78	07.58	06.19
9	4.326	4.267	06.07	05.85	05.73
10	4.114	4.058	05.79	05.62	05.26

Table 29

Adsorption of Malachite green dye on Eucalyptus wood charcoal (Particle size 150 mesh)

(a)Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.75	9.25	92.50
2	20	1.8	18.2	91.00
3	30	3.0	27.0	90.00
4	40	4.1	35.9	89.75
5	50	5.4	44.6	89.20
6	60	7.1	52.9	88.16
7	70	8.6	61.4	87.71
8	80	12.1	67.9	84.87
9	90	16.1	73.9	82.11
10	100	20.8	79.2	79.20

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	1.1	8.9	89.00
2	20	2.5	17.5	87.50
3	30	4.1	25.9	86.33
4	40	5.5	34.5	86.25
5	50	6.9	43.1	86.20
6	60	8.4	51.6	86.00
7	70	10.1	59.9	85.57
8	80	14.0	66.0	82.50
9	90	17.9	72.1	80.11
10	100	21.8	78.2	78.20

initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 29a). The corresponding values of free energy (-ΔG) were 6.417, 5.965, 5.704, 5.643, 5.514, 5.287, 5.194, 4.679, 4.263 and 3.890 $kJmole^{-1}$(table 30). At temperature of 30^0C, the adsorption were 89.00, 87.50, 86.33, 86.25, 86.20, 86.00, 85.57, 82.50, 80.11, and 78.20 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 29b). The corresponding values of free energy were 5.652, 5.324, 5.096, 5.080, 5.071, 5.034, 4.957, 4.463, 4.135 and 3.900 $kJmole^{-1}$ respectively in the same order (table 30) of initial dye concentration. The respective values of enthalpy (-ΔH) were 29.22, 25.06, 23.83, 22.41, 18.70, 12.83, 12.26, 11.12, 8.08 and 3.58 $kJmole^{-1}$ and entropy (-ΔS) values were 76.53, 64.10, 60.42, 56.28, 44.26, 25.31, 23.73, 21.64, 2.83, and 1.03 $K^{-1}J\ mole^{-1}$(table 30). The values of K were 13.32, 11.12, 9.99, 9.74, 9.25, 8.44, 8.13, 6.60, 5.58, and 4.80 in the same order of increasing initial dye concentration.

Effect of Concentration :- The results in table 27a and 27b showed that the adsorption of Malachite Green decreased from 94.00 to 81.00% by increasing dye concentration from $1x10^{-3}$ to

Table 20

Thermodynamic Parameters of Malachite green dye (Particle size – 150 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H	- Δ S (K^{-1}Jmoe^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C	(kJ Mole^{-1})		
1	6.417	5.652	29.22	76.53	13.32
2	5.965	5.324	25.06	64.10	11.12
3	5.704	5.096	23.83	60.82	09.99
4	5.643	5.080	22.41	56.28	09.74
5	5.514	5.071	18.70	44.26	09.25
6	5.287	5.034	12.83	25.31	08.44
7	5.194	4.957	12.26	23.73	08.13
8	4.679	4.463	11.12	21.64	06.60
9	4.263	4.135	08.08	12.83	05.58
10	3.890	3.690	03.58	01.03	04.80

$1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 180 mesh) and at temperature 30^0C the adsorption decreased from 91.00 to 79.50 % by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The curves at both temperatures showed decreased in adsorption with the increasing dye concentration (fig 24). The curves at both temperatures were found to be smooth and continuous.

The results in table 29a and 29b showed that the adsorption of Malachite green decreased from 91.00 to 79.20 % by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 150 mesh) and at temperature 30^0C, adsorption decreased from 89.00 to 78.20% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The curves at both temperatures showed decreased in adsorption with the increase of initial dye concentration (fig 25). The curves at both temperatures were found to be smooth and continuous in nature.

Effect of particle size :- The results in table 29a and 27a showed that the adsorption of Malachite green increased from 79.20-91.00% to 81.00-

94.00 % with decrease in particle size from 150 to 180 mesh at a temperature 20^{0}C. At a temperature of 30^{0}C, results showed that adsorption increased from 80.11-89% to 79.50-91.00% with decrease in particle size from 150-180 mesh (table 29b and 27b). It was observed that adsorption increased with decrease in particle size.

Effect of Temperature: - The results indicated from table (27a and 27b) that the adsorption of Malachite green decreased from 94.60-81.00% to 91.00-79.50 % with increase in temperature from 20^{0}C to 30^{0}C for particle size 180 mesh. For particle size 150 mesh, results indicated that percent adsorption of Malachite green decreased from 91.00-79.20% to 89.00-78.20 % with increase in temperature from 20^{0}C to 30^{0}C (table 29a and 29b). It was observed that adsorption decreased with the rise of temperature.

It was found that free energy (-ΔG) decreased from 6.920-4.114 to 6.166-4.058 kJmole^{-1} with increasing temperature from 20^{0}C to 30°C for particle size 180 mesh, and for particle size 150 mesh (-ΔG) decreased from 6.417-3.890 to 5.652-3.900 kJmole^{-1} with increasing temperature from 20^{0}C to 30^{0}C. The values of entropy (-ΔS) and

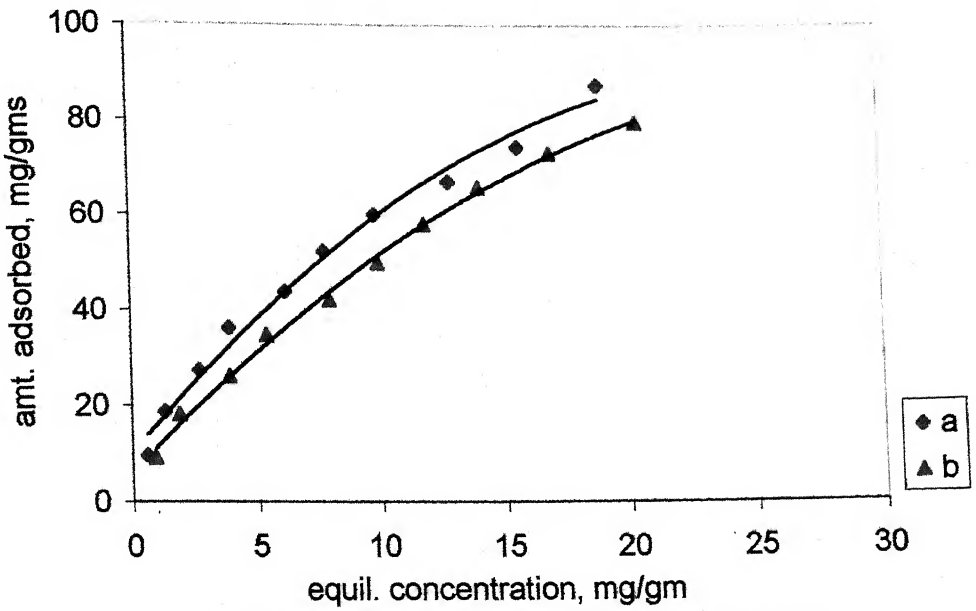


fig 24 Equilibrium isotherm of Malachite Green
(Particle Size 180 mesh) a - 20°C, b- 30°C

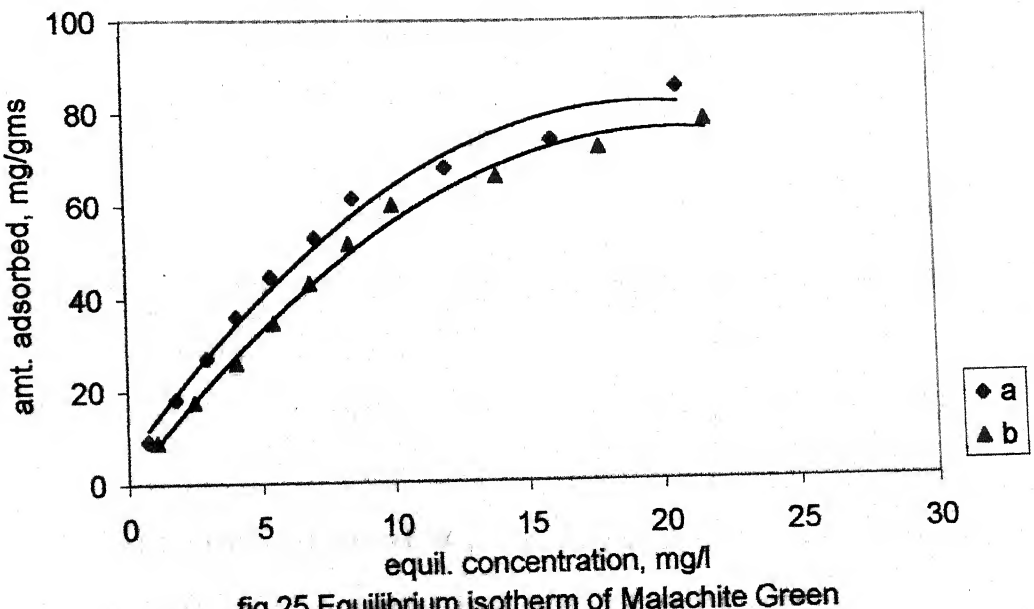


fig 25 Equilibrium isotherm of Malachite Green
(Particle Size 150 Mesh) a - 20°C, b - 30°C

enthalpy (-ΔH) change were found to be negative (table 35, 37).

Adsorption Isotherm :- The results favoured the adsorption of Malachite green on eucalyptus wood charcoal at different temperatures obeyed Freundlich adsorption isotherm. The data were fitted to the linear form of Freundlich equation

$$\ln qe = \ln K_f + (1/n) \ln Ce$$

The plot (fig 26, 27) of ln qe versus log Ce for various initial concentrations was found to be linear indicating the applicability of Freundlich adsorption isotherm .For particle size 180 mesh at 20^0C ,the values of K_f and 1/n was 2.69 and 0.605 respectively. Similarly, at 30^0C the value of K_f and 1/n was 2.31 and 0.679 respectively. It was clear that (table 32) for particle size 150 mesh at 20^0C the value of K_f and 1/n was 2.51 and 0.679 respectively. Similarly, at 30^0C the value of K_f and 1/n was 2.16 and 0.755 respectively. It was found that the value of K_f decreased with the rise of temperature showing that the rate of adsorption also decreased with rise of temperature.

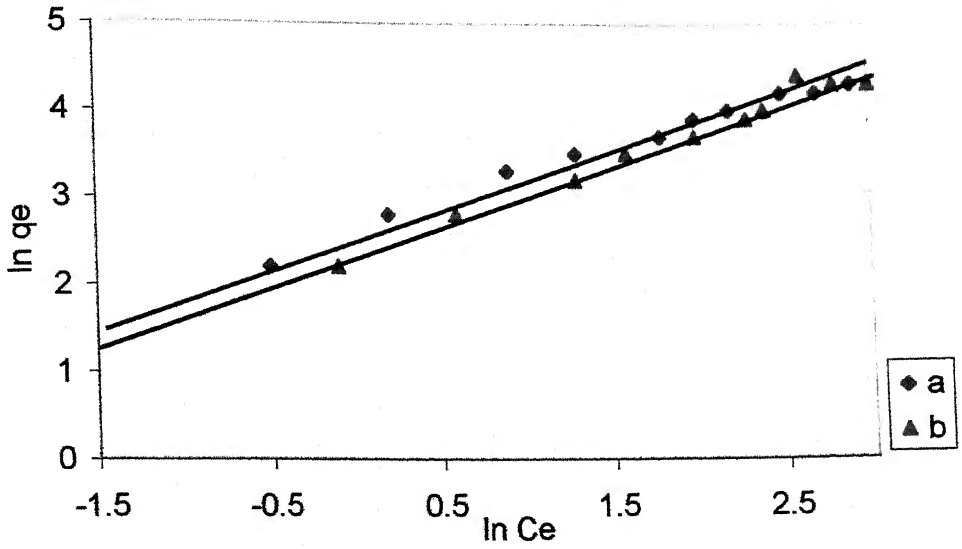


Fig 26 Freundlich adsorption isotherm of Malachite Green
a-20 °C b-30 °C (Particle size 180 mesh)

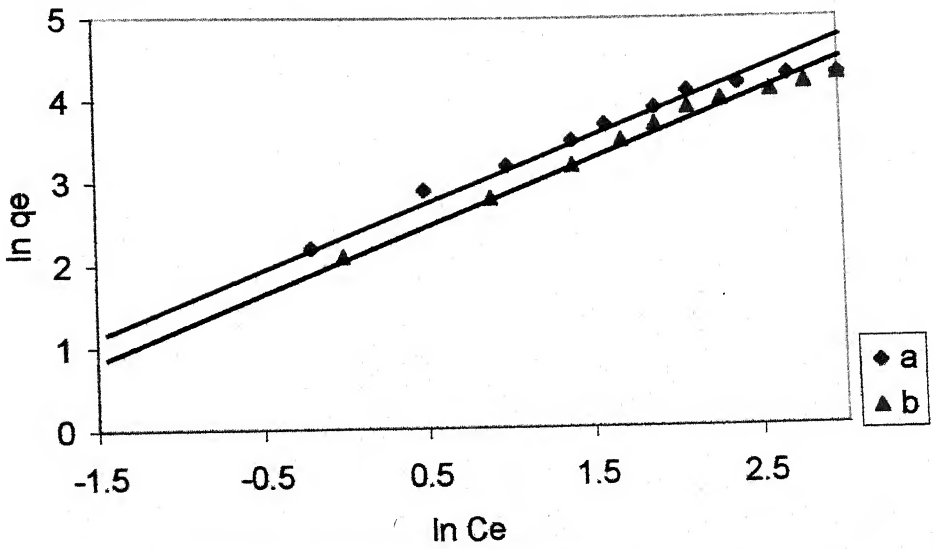


Fig 27 Freundlich adsorption isotherm of Malachite Green
a-20 °C b-30 °C (Particle size 150 mesh)

Effect of pH :- The effect of pH on the adsorption of Malachite green dye showed in fig 23. The percent adsorption of Malachite green dye were 30.40, 41.60, 54.30, 64.00, 68.40, 78.00, 87.20, 90.80, 93.20, and 85.60 with increasing pH values from 2.5 to 11.5 and temperature 30^0C and concentration 25 mg/l (table 31). It was observed that with the increased of pH from 2.5 to 10.5 the adsorption of Malachite green increase from 30.40 to 93.20 % by eucalyptus wood charcoal and above the pH of 10.5, the adsorption was found to decrease gradually.

Table 31

Adsorption of Malachite Green at different Temperature 30 °C, Initial dye concentration 25 mg/l

S No	pH	Equilibrium dye concentration (mg/l)	Amount of dye adsorbed (mg/gm)	% adsorption
1	2.5	17.4	7.6	30.40
2	3.5	14.6	10.4	41.60
3	4.5	11.3	13.7	54.80
4	5.5	9.0	16.0	64.00
5	6.5	7.9	17.1	68.40
6	7.5	5.5	19.5	78.00
7	8.5	3.2	21.8	87.20
8	9.5	2.3	22.7	90.80
9	10.5	1.7	22.3	93.20
10	11.5	3.6	21.4	85.60

Table 32

Freundlich Constant for Malachite green

Particle Size	Temperature	K_f	1/n
180 Mesh	20^0 C	2.64	0.605
	30^0 C	2.31	0.679
150 Mesh	20^0 C	2.51	0.679
	30^0 C	2.16	0.755

fig 28 Adsorption of Malachite Green at different pH, Temperature 30 °C, Initial dye concentration 25 m/l

Rhoda mine

The adsorption of Rhoda mine on eucalyptus wood charcoal was found to be 81.60, 83.60, 84.00, 85.20, 86.80, 87.60, 88.00, 89.60, 90.00, and 91.60 percent for the initial dye concentration 25 mg/l with the increasing contact time 5,10,20,..... to 90 min respectively and for initial dye concentration 50mg/l the percentage adsorption was 77.00, 79.40, 80.00, 81.00, 83.40, 85.00, 86.20, 87.20, 88.00, and 88.60 with the increasing contact time 5,10,20,.....90 min at temperature 30^0C and pH 7.5 respectively. Similarly, for initial dye concentration 75 mg/l the adsorption was found to be 73.60, 76.53, 78.26, 79.20, 80.80, 81.46, 82.26, 84.66, 85.33, and 86.40 with the increasing contact time 5,10,20,.....90 min respectively(table 33).

Effect of contact time :- fig 29 showed the effect of dye concentration on the extent of adsorption as a function of time for the initial dye concentration of 25,50,75mg/l. It was found that the amount of dye adsorbed increased from 20.4 to 22.9, 38.5 to 44.3, 55.2 to 64.8 mg/l respectively with the increase of time and achieved equilibrium

Table 33 Kinetic study of Rhodamine B on eucalyptus wood charcoal at different concentration and pH=7.5 and T=30°C

s	time	initial concentration of dye		initial concentration of dye		initial concentration of dye	
no.	(min)	(25 mg/l)		(50 mg/l)		(75 mg/l)	
		amount adsorbed	% adsorption	amount adsorbed	% adsorption	amount adsorbed	% adsorption
		(mg/gms)		(mg/gms)		(mg/gms)	
1	5	20.4	81.6	38.5	77.0	55.2	73.6
2	10	20.9	83.6	39.7	79.3	57.6	76.5
3	20	21.0	84.0	40.0	80.0	58.7	78.2
4	30	21.3	85.2	40.5	81.0	59.4	79.2
5	40	21.7	86.8	41.7	83.4	60.6	80.8
6	50	21.9	87.6	42.5	85.0	61.1	81.5
7	60	22.0	88.0	43.0	86.0	61.7	82.3
8	70	22.4	89.6	43.6	87.2	63.5	84.6
9	80	22.5	90.0	44.0	88.0	64.0	85.3
10	90	22.9	91.6	44.3	88.6	64.8	86.4

in 90 min at temperature 30^0C and pH 7.5, after wards no significant change was found. The time variation curves of adsorption were found to be smooth and continuous.

Adsorption dynamics :- The straight line plot of log (qe-q) versus t for Rhodamine adsorption by eucalyptus wood charcoal at 30^0C (fig 30) indicated the applicability of Lagergren equation. The values of rate constant (K_{ad}) was $1.92x10^{-2}$, $2.36x10^{-2}$, $1.97x10^{-2}$ min^{-1} for an initial concentration of 25,50 and 75 mg/l respectively at temperature 30^0C and pH 7.5. The plot was linear for a wide range of concentrations and contact period.

The adsorption of Rhodamine B, on eucalyptus wood charcoal (particle size-180 mesh) at temperature 20^0C were 90.09, 89.50, 88.33, 87.00, 86.00, 84.83, 83.57, 83.00, 81.22, and 80.40 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}(table-34a). The corresponding values of free energy ($-\Delta G$) were 5.938, 5.583, 5.322, 5.057, 4.871, 4.672, 4.474, 4.390, 4.143, and 4.037 kJ $mole^{-1}$ (table 35). At

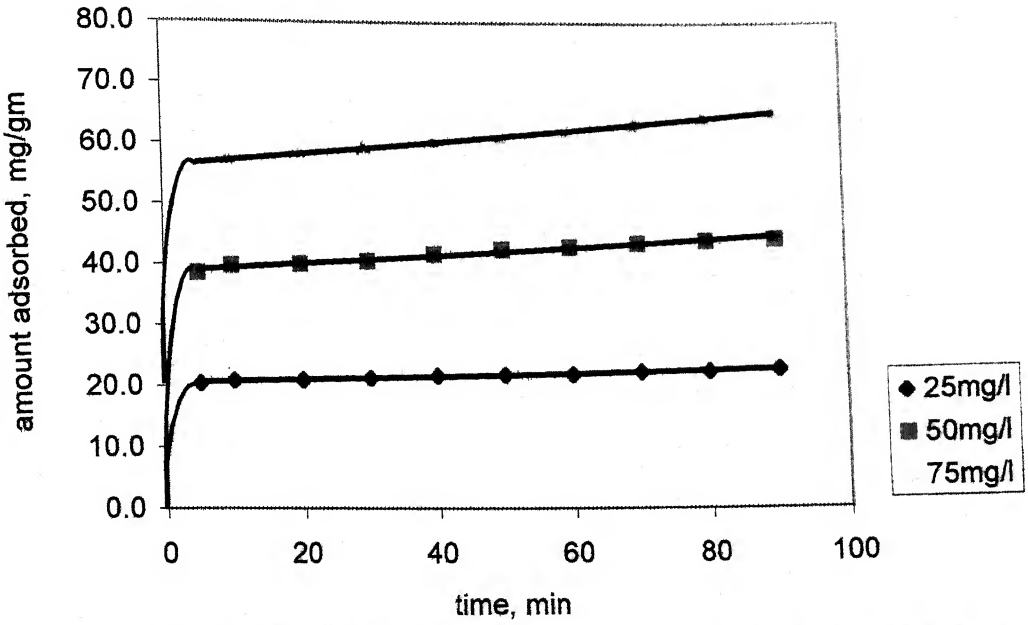


fig :29 Effect of concentration and contact time on adsorption of Rhodamine B on eucalyptus wood charcoal at pH=7.5 and T=30°C

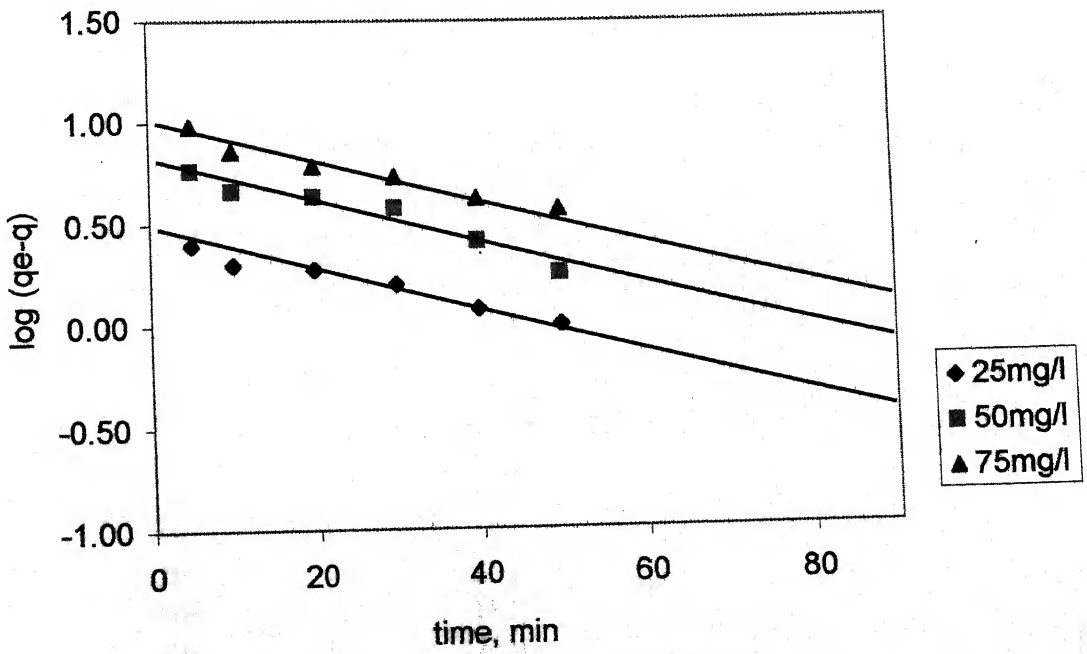


fig 30. Lagergren plot for Rhodamine B

Table 34

Adsorption of RhodamineB dye on Eucalyptus wood charcoal (Particle size 180 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.91	9.09	90.09
2	20	2.1	17.9	89.50
3	30	3.5	26.5	88.33
4	40	5.2	34.8	87.00
5	50	7.0	43.0	86.00
6	60	9.1	50.9	84.83
7	70	11.5	58.5	83.57
8	80	13.6	66.4	83.00
9	90	16.9	73.1	81.22
10	100	19.6	80.4	80.40

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2gm)	% Adsorption
1	10	1.2	8.8	88.00
2	20	2.6	17.4	87.00
3	30	4.2	25.8	86.00
4	40	6.1	33.9	84.75
5	50	8.1	41.9	83.80
6	60	10.5	49.5	82.50
7	70	13.1	56.9	81.28
8	80	15.0	65.0	81.25
9	90	18.2	71.8	79.77
10	100	21.0	79.0	79.00

temperature 30^0C the percent adsorption of Rhodamine B were 88.00, 87.00, 86.00, 84.75, 83.80, 82.50, 81.28, 81.25, 79.77, and 79.00 for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 34b). The corresponding values of free energy ($-\Delta G$) were 5.429, 5.224, 5.034, 4.815, 4.660, 4.463, 4.291, 4.286, 4.093 and 3.996, kJ $mole^{-1}$ (table 35).

The respective values of enthalpy ($-\Delta H$) were 21.10, 16.29, 13.91, 12.18, 11.37, 10.91, 9.94, 7.47, 5.65 and 5.26 $kJmole^{-1}$ and entropy values ($-\Delta S$) were 50.87, 35.92, 28.81, 23.91, 20.93, 18.34, 10.33, 5.03 and 4.10 $K^{-1}Jmole^{-1}$ (table 35). The values of K are 10.98, 9.51, 8.56, 7.68, 7.13, 6.58, 6.08, 5.88, 5.32, and 5.09, in the same order of increasing initial dye concentration (table 35).

For particle size 150 mesh, the adsorption of Rhodamine B at temperature 20^0C were 87.00, 85.50, 85.33, 84.75, 82.40, 81.60, 80.85, 79.12, 77.77, and 76.00 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 36a). The corresponding values of free energy ($-\Delta G$) were 5.054, 4.784, 4.755, 4.659, 4.304, 4.202, 4.095, 3.881, 3.726, and 3.535, $kJmole^{-1}$ (table 37). At temperature 30^0C, the adsorption

Table 35

Thermodynamic Parameters for Rhodamine B dye (particle size – 180 mesh)

Sr. No	-Δ G (kJMole^{1})		- Δ H	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C	(k JMole)		
1	5.938	5.429	21.10	50.87	10.98
2	5.583	5.224	16.29	35.92	09.51
3	5.322	5.034	13.91	28.81	08.56
4	5.054	4.815	12.18	23.91	07.68
5	4.871	4.660	11.37	21.80	07.13
6	4.672	4.463	10.91	20.93	06.58
7	4.474	4.291	09.94	18.34	06.08
8	4.390	4.286	07.47	10.33	05.88
9	4.143	4.093	05.65	05.05	05.32
10	4.037	3.996	05.26	04.10	05.09

Table 36

Adsorption of Rhodamine B dye on Eucalyptus wood charcoal (particle size –150 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	1.3	8.7	87.00
2	20	2.9	17.1	85.50
3	30	4.4	25.6	85.33
4	40	6.1	33.9	84.75
5	50	8.8	41.2	82.40
6	60	11.0	49.0	81.66
7	70	13.4	56.6	80.85
8	80	16.7	63.3	79.12
9	90	20.0	70.0	77.77
10	100	24.0	76.0	76.00

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0. 2 gm)	% Adsorption
1	10	1.6	8.4	84.00
2	20	3.4	16.6	83.00
3	30	5.1	24.9	83.00
4	40	7.0	33.0	82.50
5	50	9.8	40.2	80.40
6	60	12.1	47.9	79.83
7	70	14.6	55.4	79.14
8	80	18.0	62.0	77.50
9	90	21.5	68.5	76.11
10	100	25.1	74.9	74.90

were 84.00, 83.00, 83.00, 82.50, 80.40, 79.83, 79.14, 77.50, 76.11, and 74.90, percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (table 36b). The corresponding values of free energy ($-\Delta G$) were 4.692, 4.537, 4.537, 4.463, 4.173, 4.100, 4.013, 3.819, 3.666, 3.539, $kJmole^{-1}$(table37) The respective values of enthalpy ($-\Delta H$) were 15.84, 12.13, 11.26, 10.50, 8.21, 7.27, 6.54, 5.72, 5.51, and 3.41 $kJmole^{-1}$ and entropy ($-\Delta S$) values were 36.19, 24.65, 21.84, 19.60, 13.10, 10.29, 8.20, 6.17, 5.98, 0.41, $K^{-1}Jmole^{-1}$ (table 37) The values of K were 7.68, 6.89, 6.81, 6.55, 5.67, 5.45, 5.22, 4.78, 4.49, and 4.16, in the same order of increasing initial dye concentration. (table 37).

Effect of concentration :- The result showed (table 34a and 34b) that the adsorption of Rhodamine B decreased from 90.09 to 80.40 % by increasing initial dye concentration $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 180 mesh) and at temperature 30^0C the adsorption decreased from 88.00 to 79.00% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The curves at both temperatures showed that the adsorption decreased with increasing dye

Table 37

Thermodynamic Parameters for Rhodamines-B dye (Particle size – 150 Mesh)

Sr. No	-ΔG(kJ Mole^{-1})		- Δ H	- Δ S ($K^{-1}Jmole^{-1}$)	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C	(kJ Mole^{-1})		
1	5.054	4.692	15.84	36.19	07.68
2	4.784	4.537	12.13	24.65	06.89
3	4.755	4.537	11.26	21.84	06.81
4	4.659	4.463	10.50	19.60	06.55
5	4.304	4.173	08.21	13.10	05.67
6	4.202	4.100	07.27	10.29	05.45
7	4.095	4.013	06.54	08.20	05.22
8	3.881	3.819	05.72	06.17	04.78
9	3.726	3.666	05.51	05.98	04.49
10	3.535	3.539	03.41	00.41	0.416

concentration (fig 31). The curves at both temperatures were found to be smooth and continuous in nature.

The results showed (table 36a and 36b) that the adsorption of Rhodamine B decreased from 87.00 to 76.00% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} at temperature 20^0C(particle size 150 mesh) and at temperature 30^0C, adsorption decreased from 84.00 to 74.90% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}. The curves at both temperatures showed that the adsorption decreased with increasing dye concentration (fig 32). The curves at both temperatures were found to be smooth and continuous in nature.

Effect of particle size :- The results showed (table 36a and 34a) that the adsorption of Rhodamine B increased form 76.00-87.00% to 80.40-90.09% with decrease in particle size from 150-180 mesh and at temperature 20^0C. At temperature of 30^0C, results showed (table 36b and 34b) that the adsorption increased with decrease in particle size.

Effect of temperature: - The results indicated (table 34a and 34b) that the adsorption of Rhoda mine B decreased from 90.09-80.40 % to 88.00-79.00% with increasing temperature 20^0C to 30^0c for particle size 180 mesh. For particle size 150mesh, results (table 36a and 36b) indicated that percent adsorption of RhodamineB decreased from 87.00-76.00% to 84.00-74.90 with increasing temperature 20^0C to 30^0C. It was observed that adsorption decreased with the rise of temperature. The results also indicated that the free energy (-ΔG) decreased from 5.938-4.037 to 5.429-3.996 kJmole^{-1} with increasing temperature 20^0C to 30^0C for particle size 180 mesh and for particle size 150 mesh the free energy decreased from 5.054-3.535 to 4.692-3.539 kJmole^{-1} with increasing temperature 20^0C to 30^0C(table 37). The values of entropy (ΔS) and enthalpy (ΔH) change were found to be negative.

Adsorption Isotherms: - The results showed that the adsorption of RhodamineB on eucalyptus wood charcoal at different temperatures obeyed Freundlich adsorption isotherm. The data were fitted to the linear form of Freundlich equation .

$\ln qe = \ln K_f + 1/n \ln Ce$

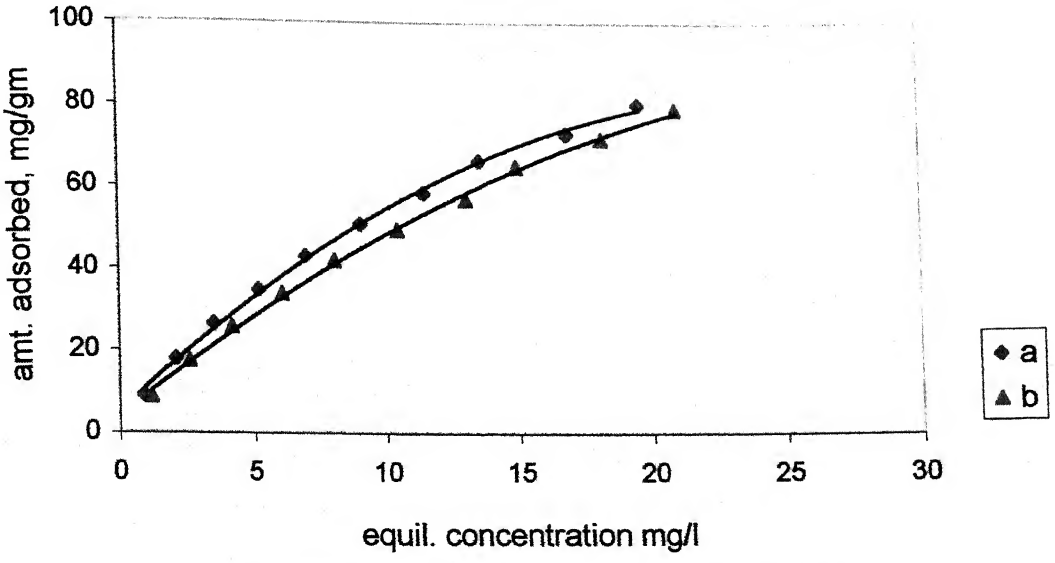


fig 31 Equilibrium isotherm of Rhodamine B
(Particle size 180 mesh) a - 20°C, b - 30°C

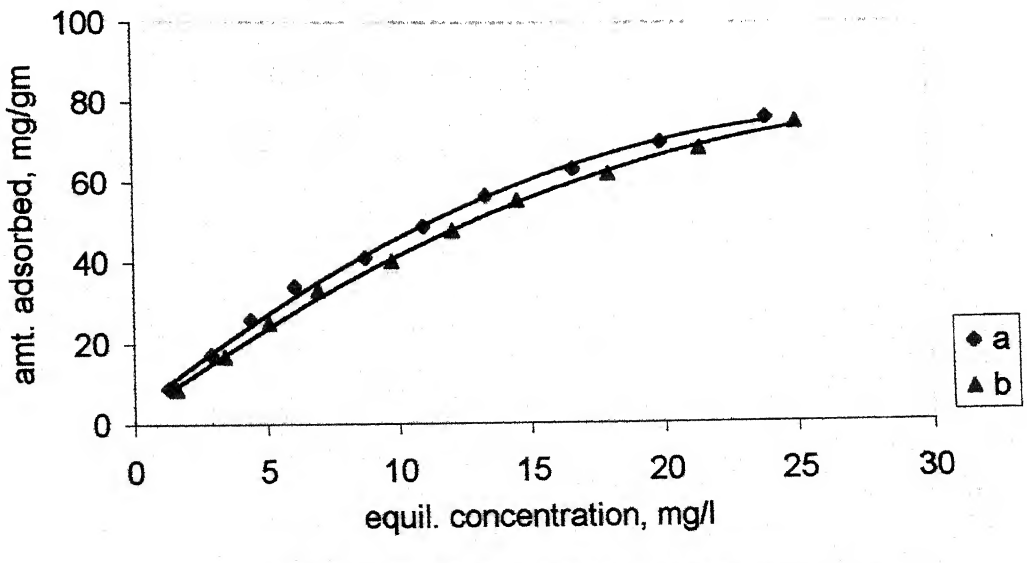


fig 32 Equilibrium isotherm of Rhodamine B
(Particle Size 150 Mesh) a - 20°C, b - 30°C

The plot of ln qe versus ln Ce for various initial concentration was found to be linear, indicating the applicability of Freundlich adsorption isotherm (fig 33, 34). For particle size 180 mesh, at 20^0C the values of K_f and 1/n was 2.32, 0.685 respectively. Similarly, the values of K_f and 1/n at 30^0C was 2.12, 0.735 respectively .For particle size 150 mesh ,at 20^0C the values of K_f and 1/n was 2.02, 0.764 respectively. Similarly, at 30^0C the value of K_f and 1/n was 1.85, 0.795 respectively. It was clear from the table 39, that the value of K_f decreased with the rise of temperature showing that the rate of adsorption also decreased with rise of temperature.

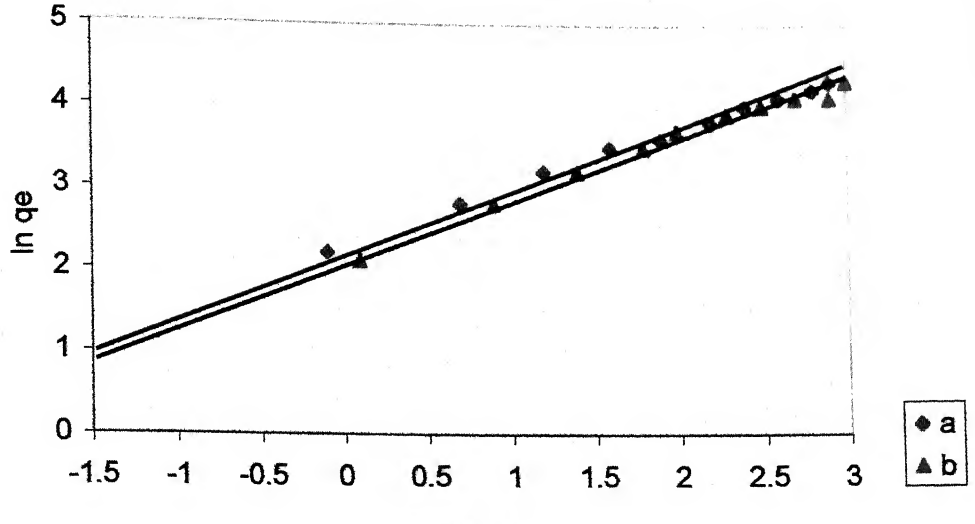


Fig 33 Freundlich adsorption isotherm of Rhodamine B
a-20 °C b-30 °C (Particle size- 180 Mesh)

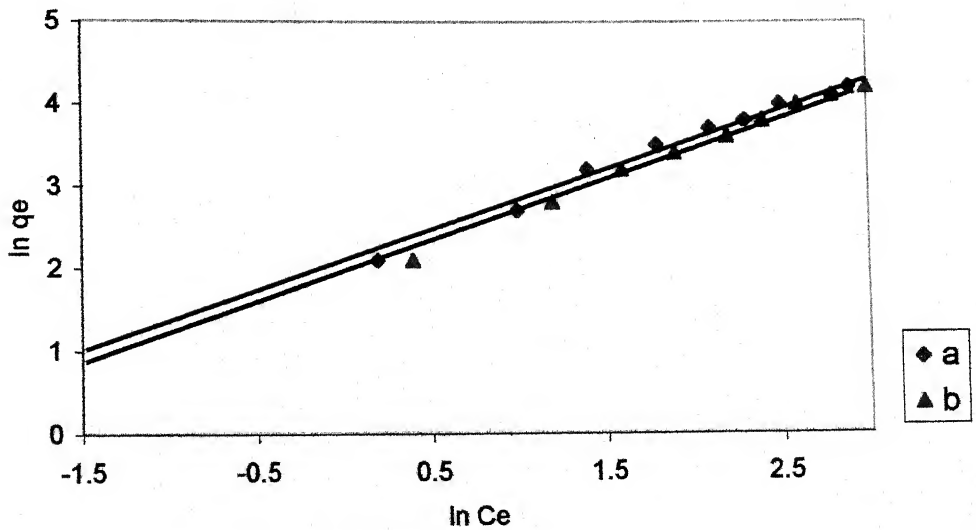


Fig 34 Freundlich adsorption isotherm of Rhodamine B
a-20 °C b-30 °C (Particle size- 150 Mesh)

Effect of pH: - The effect of pH on the adsorption of Rhodamine B dye was showed in (fig 33) . The percent adsorption of Rhodamine B dye were 29.20, 38.00, 44.40, 57.60, 65.20, 76.00, 79.60, 82.40, 89.20, and 83.60, with increasing pH values from 2.5 to 11.5 at temperature 30^0C and concentration 25 mg/l (table 38). It was observed that with the increased of pH from 2.5 to 10.5 the adsorption of Rhodamine B dye increased from 29.20 to 89.20% by eucalyptus wood charcoal and above the pH of 10.5 the adsorption was found to decrease gradually.

Table 38

Adsorption of Rhodamine B at Different pH, Temperature 30 °C, Initial Concentration 25 mg/l

S No	pH	Equilibrium dye concentration (mg/l)	Amount of dye adsorbed (mg/gm)	% adsorption
1	2.5	17.7	7.3	29.20
2	3.5	15.5	9.5	38.00
3	4.5	13.9	11.1	44.40
4	5.5	10.6	14.4	57.60
5	6.5	8.7	16.3	65.20
6	7.5	6.0	19.0	76.00
7	8.5	5.7	19.9	79.60
8	9.5	4.4	20.6	82.40
9	10.5	2.7	22.3	89.20
10	11.5	4.1	20.9	83.60

Table 39

Freundlich Constant for Rhodamine B

Particle Size	Temperature	K_f	1/n
180 Mesh	20^0 C	2.32	0.685
	30^0 C	2.12	0.735
150 Mesh	20^0 C	2.02	0.764
	30^0 C	1.85	0.795

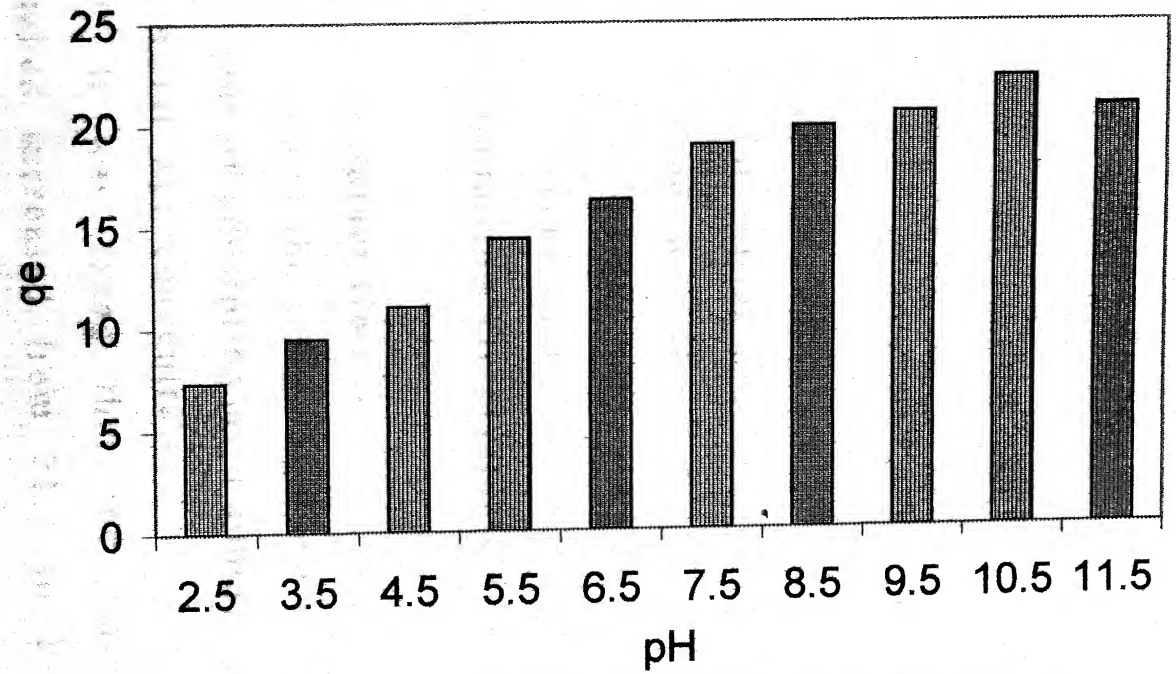


fig 33 Adsorption of Rhodamine B at different pH, Temperature 30 ^{0}C, Initial concentration 25 mg/l

Aniline Blue

When the initial dye concentration was 25 mg/l, the adsorption of Aniline Blue on Eucalyptus wood charcoal was found to be 84.40, 85.20, 86.40, 87.20, 88.40, 90.40, 91.20, 92.40, 93.20, and 93.60 percent with the increasing contact time of 5,10,20,.....,90min respectively and for initial dye concentration 50mg/l the percent adsorption of dye was 80.00, 81.80, 83.20, 84.80, 86.60, 86.80, 88.00, 89.20, 90.20 and 91.20 with the increasing contact time from 5,10,20,....,90 min respectively at temperature 30^0C and pH 7.5. Similarly, for initial dye concentration 75 mg/l the adsorption was found to be 77.46, 78.93, 79.73, 82.13, 83.86, 85.73, 87.33, 88.00, 88.93, and 89.20 percent with the increasing time 5, 10, 20, ..., 90min respectively(table 40).

Effect of Contact time :-

Fig 34 showed the effect of dye concentration on the extent of adsorption as a function of time for the initial dye concentration of 25, 50, and 75 mg/l. It was found that the amount of dye adsorbed increased from 21.1 to 23.4, 40.0 to 45.4, 58.1 to 67.7 mg/gm for the initial dye

Table 40 Kinetic study of Aniline blue on eucalyptus wood charcoal at different concentration and pH=7.5 and T=30°C .

s no.	time (min)	initial concentration of dye (25 mg/l)		initial concentration of dye (50 mg/l)		initial concentration of dye (75 mg/l)	
		amount adsorbed (mg/gms)	% adsorption	amount adsorbed (mg/gms)	% adsorption	amount adsorbed (mg/gms)	% adsorption
1	5	21.1	84.4	40.0	80.0	58.1	77.4
2	10	21.3	85.2	40.9	81.8	59.2	78.9
3	20	21.6	86.4	41.6	83.2	59.8	79.7
4	30	21.8	87.2	42.4	84.8	61.6	82.1
5	40	22.1	88.4	43.3	86.6	62.9	83.8
6	50	22.6	90.4	43.4	86.8	64.3	85.7
7	60	22.8	91.2	44.0	88.0	65.5	87.3
8	70	23.1	92.4	44.6	89.2	66.0	88.0
9	80	23.3	93.2	45.1	90.2	66.4	88.9
10	90	23.4	93.6	45.4	91.2	67.7	89.2

concentration of 25, 50, and 75mg/l respectively with the increase of contact time and achieved equilibrium in 90 min at temperature 30^0C and pH 7.5, afterwards no significant change was found. The time variation curves of adsorption were found to be smooth and continuous.

Adsorption Dynamics :-

The straight line plot log (qe-q) versus t for Aniline Blue adsorption by eucalyptus wood charcoal at 30^0C (fig35) indicated the applicability of Lagergren equation. The values of rate constant (K_{ad}) was $2.12x10^{-2}$, $2.29x10^{-2}$, and $2.21x10^{-2}$ min^{-1} for initial dye concentration of 25,50, and 75 mg/l respectively at temperature 30^0C and pH 7.5. The plot was linear for a wide range of concentrations and contact period.

The adsorption of Aniline Blue on Eucalyptus wood charcoal at temperature 20^0C (particle size 180 mesh) were 93.00, 90.50, 87.66, 85.00, 84.40, 83.00, 81.57, 80.75, 79.88 and 79.00 percent for increasing initial dye concentration from $1x\ 10^{-3}$ to $1x10^{-2}$ mgl^{-1} (Table 41a). The corresponding values of free energy were 6.588, 5.831, 5.185,

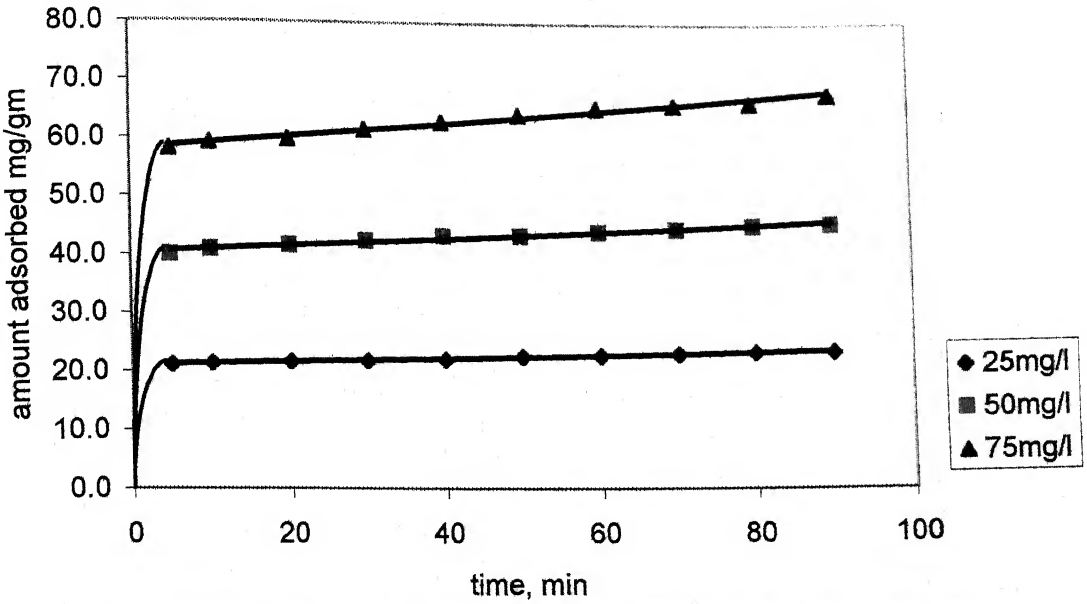


fig 34 Effect of concentration and time on adsorption of Aniline blue on eucalytpus wood charcoal at pH=7.5 and T=30°C

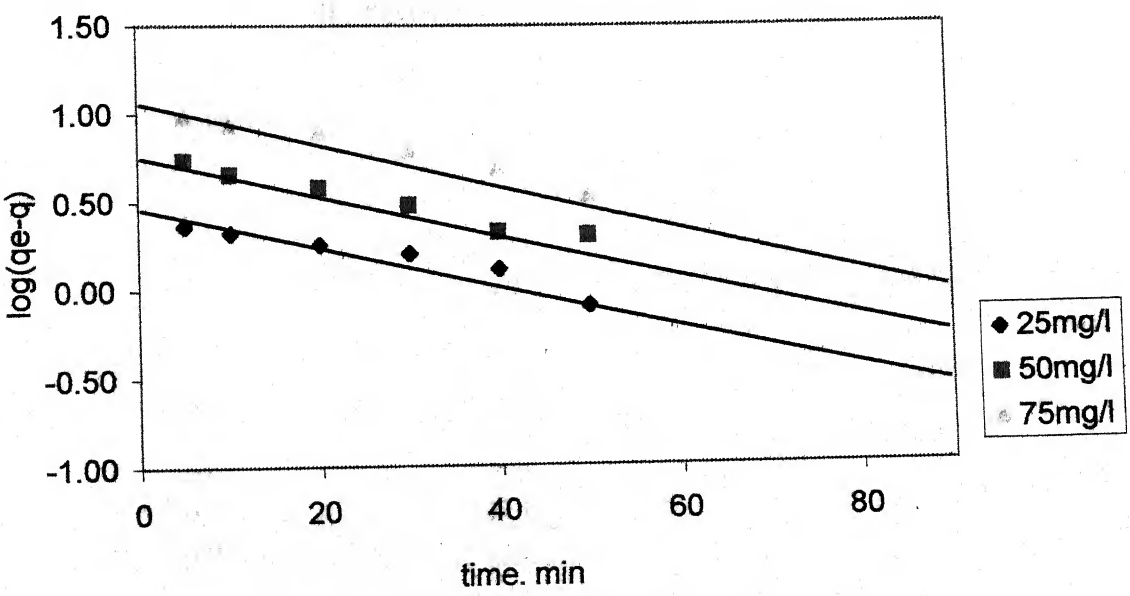


fig 35. Lagergren plot for Aniline blue

Table 41

Adsorption of Aniline Blue dye on Eucalyptus wood charcoal (Particle size 180 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.7	9.3	93.00
2	20	1.9	8.1	90.50
3	30	3.7	26.3	87.66
4	40	6.0	34.0	85.00
5	50	7.8	42.2	84.40
6	60	10.2	49.8	83.00
7	70	12.9	57.1	81.57
8	80	15.4	64.6	80.75
9	90	18.1	71.9	79.88
10	100	21.0	79.0	79.00

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0. 2 gm)	% Adsorption
1	10	1.0	9.0	90.00
2	20	2.6	17.4	87.00
3	30	4.8	25.2	84.00
4	40	7.5	32.5	81.25
5	50	9.4	40.6	81.20
6	60	12.0	48.0	80.00
7	70	15.0	55.0	78.57
8	80	17.2	62.8	78.50
9	90	20.1	69.9	77.66
10	100	22.8	77.2	77.20

4.700, 4.603, 4.390, 4.190, 4.082, 3.973, 3.866 $kJmole^{-1}$ (Table 42). At temperature of 30°C the percent adsorption of Aniline blue were 90.00, 87.00, 81.25, 81.20, 80.00, 78.57, 78.50, 77.66 and 77.20 for increasing initial dye concentration $1x10^{-3}$ to $1x10^{-2}mgl^{-1}$ (Table 41b). The corresponding values of free energy were 5.896, 5.224, 4.692, 4.286, 4.279, 4.121, 3.944, 3.936, 3.838 and 3.785 $kJmol^{-1}$ (Table 42). The respective values of enthalpy were 27.21, 23.93, 19.86, 17.02, 14.23, 12.40, 11.50, 8.43, 7.99 and 6.27 $kJmol^{-1}$ and entropy values were 69.22, 60.74, 41.36, 32.33, 26.88, 24.56, 14.60, 13.50 and 8.08 $K^{-1}Jmole^{-1}$. The values of K were 14.27, 10.51, 8.10, 6.66, 6.40, 5.88, 5.42, 5.19, 4.96, 4.75 in the same order of increasing initial dye concentration (Table 42). For particle size 150 mesh, the adsorption of Aniline Blue at temperature 20^0C were 91.80, 91.50, 89.33, 87.25, 85.60, 85.00, 84.00, 82.62, 80.44 and 78.50 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1} (Table 43a). The corresponding values of free energy were 5.472, 5.429, 4.974, 4.537, 4.362, 4.275, 4.158, 4.042, 3.877 and 3.774 $kJmol^{-1}$(Table 44). At temperature 30^0C, adsorption were 88.20, 88.00, 85.66, 83.00,

Table 42

Thermodynamic Parameters of Aniline Blue dye (Particle size – 180 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 °C	Tem – 30 °C			
1	6.588	5.896	27.21	69.22	14.27
2	5.831	5.224	23.93	60.74	10.51
3	5.185	4.692	19.86	49.24	08.10
4	4.700	4.286	17.02	41.36	06.66
5	4.603	4.279	14.23	32.33	06.40
6	4.390	4.121	12.40	26.28	05.88
7	4.190	3.944	11.50	24.56	05.42
8	4.082	3.936	08.43	14.60	05.19
9	3.973	3.838	07.99	13.50	04.96
10	3.866	3.785	06.27	08.08	04.75

Table 43

Adsorption of Aniline Blue dye on Eucalyptus wood charcoal (Particle size 150 mesh)

(a) Temperature 20 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	0.82	9.18	91.80
2	20	1.7	18.3	91.50
3	30	3.2	26.8	89.33
4	40	5.1	34.9	87.25
5	50	7.2	42.8	85.60
6	60	9.0	51.0	85.00
7	70	11.2	58.8	84.00
8	80	13.9	66.1	82.62
9	90	17.6	72.4	80.44
10	100	21.5	78.5	78.50

(b) Temperature 30 ^{0}C

Sr. No	Initial dye concentration ($1x10^{-4}$ mg/l)	Equilibrium dye concentration ($1x10^{-4}$ mg/l)	Amount of dye adsorbed (mg/0.2 gm)	% Adsorption
1	10	1.18	8.82	88.20
2	20	2.4	17.6	88.00
3	30	4.3	25.7	85.66
4	40	6.8	33.2	83.00
5	50	9.1	40.9	81.80
6	60	11.3	48.7	81.16
7	70	13.8	56.2	80.28
8	80	16.5	63.5	79.37
9	90	19.8	70.2	78.00
10	100	22.9	77.1	77.10

81.80, 81.16, 79.37, 78.00 and 77.10 percent for increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ $kJmole^{-1}$ (Table 43b). The corresponding value of free energy ($-\Delta G$) were 5.472, 5.429, 4.974, 4.537, 4.362, 4.275, 4.158, 4.042, 3.877 and 3.774 $kJmole^{-1}$(table 44).The respective values of enthalpy ($-\Delta H$) were 27.77, 26.31, 22.54, 21.95, 17.87, 17.36, 15.92, 13.08, 8.98 and 4.81 $kJmole^{-1}$ and entropy($-\Delta S$) values were 72.39, 67.79, 57.03, 56.53, 43.85, 42.48, 38.18, 29.34, 16.42 and 3.37 $K^{-1}Jmole^{-1}$. The values K were 12.18, 11.75, 9.36, 7.83, 6.94, 6.66, 6.24, 5.75, 5.11 and 4.64 in the same order of increasing initial dye concentration (table 44).

Effect of concentration: -

The results showed (table 41a, 41b) that the adsorption of Aniline Blue decreased from 93.00 to 79.00% by increasing initial dye concentration from $1x10^{-3}$ to $1x10^{-2}$ mgl^{-1}at temperature 20^0C (particle size 180 mesh) and at temperature 30^0C,adsorption decreased from 90.00 to77.20% by increasing initial dye concentration. The nature of curves at both temperatures showed an increased in amount of dye adsorbed on increase

Table 44

Thermodynamic Parameters of Aniline Blue dye (Particle size – 150 mesh)

Sr. No	-Δ G (kJ Mole^{-1})		- Δ H (kJ Mole^{-1})	- Δ S (K^{-1}Jmole^{-1})	K
	Tem - 20 ^{0}C	Tem - 30 ^{0}C			
1	6.196	5.472	27.77	72.39	12.18
2	6.107	5.429	26.31	67.79	11.75
3	5.544	4.974	22.54	57.03	09.36
4	5.102	4.537	21.95	56.53	07.83
5	4.801	4.362	17.87	43.85	06.94
6	4.700	4.275	17.36	42.48	06.66
7	4.540	4.158	15.92	38.18	06.24
8	4.335	4.042	13.08	29.34	05.75
9	4.043	3.877	08.98	16.42	05.11
10	3.808	3.774	04.81	03.37	04.64

in dye concentration (fig 36). Both curves were found to be smooth and continuous in nature.

The results showed (table 43a, 43b) that the adsorption of Aniline Blue decreased from 91.80to78.50% for increasing initial dye concentration from $1x10^{-3}$ to$1x10^{-2}$ mgl^{-1} at temperature 20^0C (particle size 150 mesh) and at temperature 30^0C adsorption decreased from $1x10^{-3}$ to $1x10^{-2}mgl^{-1}$.The nature of curves at both temperatures showed an increased in amount of dye adsorbed on increase in dye concentration. Both curves (at 20^0C and 30^0C) were found to be smooth and continuous in nature (fig 37).

Effect of Particle Size :-

The results showed (table 43a and 41a) that the adsorption of Aniline Blue increased from 78.50 - 90.80 % to 79.00-93.00 % with decrease in particle size from 150 - 180 mesh at temperature 20^0C. At temperature 30^0C (43b and 41b) results showed that the adsorption increased from 77.10-88.20 % to 77.20 - 90.00 % with decrease in particle size from 150 – 180 mesh. It was observed that adsorption increased with decrease in particle size.

Effect of Temperature :-

The results indicated (Table 41a and 41b) that the adsorption of Aniline Blue decreased from 93.00-79.00 % to 90.00-77.20% with increasing temperature 20^0C to 30^0 C for particle size 180 mesh. For particle size 150 mesh, results (Table 43a and 43b) indicated that percent adsorption of Aniline Blue decreased from 91.80-78.50 % to 88.20 – 77.10 % with increasing temperature 20^0C to 30^0C. It was observed that adsorption decreased with the rise of temperature.

It was found that the free energy ($-\Delta G$) decreased from 6.588 – 3.866 to 5.896 – 3.785 kJmole^{-1} with the increasing temperature 20^0C to 30^0C for particle size 180 mesh (Table 42) and for particle size 150 mesh, free energy ($-\Delta G$) decreased from 6.196 – 3.808 to 5.472 – 3.774 kJmole^{-1} with the increasing temperature 20^0C to 30^0 C (Table 44). The values of entropy ($-\Delta S$) and enthalpy ($-\Delta H$) were found to be negative (Table42, 44).

Adsorption Isotherm: The results favoured the adsorption of Aniline Blue on eucalyptus wood charcoal at different temperatures obeyed

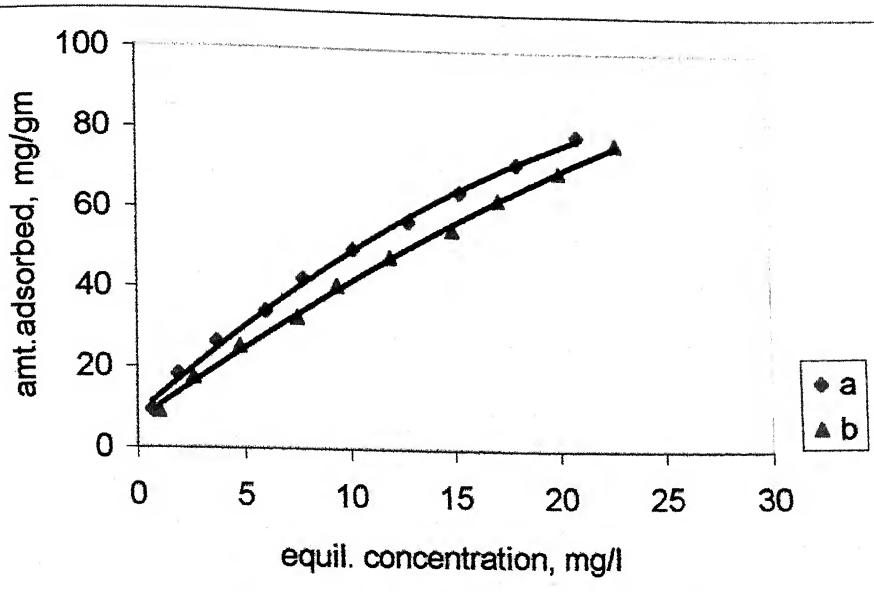


fig 36 Equilibrium isotherm of Aniline Blue
(Particle size 180 mesh) a - 20°C, b - 30°C

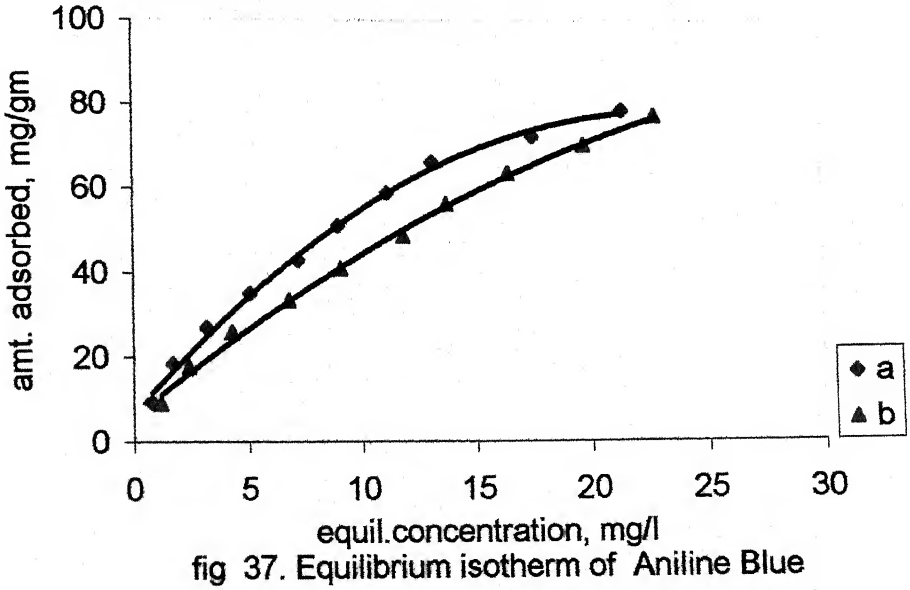


fig 37. Equilibrium isotherm of Aniline Blue
(particle size 150 mesh) a - 20°C, b - 30°C

Freundlich adsorption isotherm. The data were fitted to the linear form of Freundlich equation

$$\ln qe = \ln K_f + (1/n) \ln Ce$$

The plot of ln qe versus ln Ce for various initial concentration was found to be linear indicating the applicability of Freundlich adsorption isotherm .For particle size 180 mesh, at 20^0C the values of K_f and 1/n was 2.43,0.630 respectively. Similarly, at 30^0C the value of K_f and 1/n was 2.11 and 0.708 respectively. It was clear from the (table 46) for particle size 150 mesh at 20^0C the value of K_f and 1/n was 2.46 and 0.639 respectively. Similarly, at 30^0C the value of K_f and 1/n was 2.23 and 0.710 respectively. It was found that the value of K_f decreased with the rise of temperature showing that the rate of adsorption also decreased with rise of temperature.

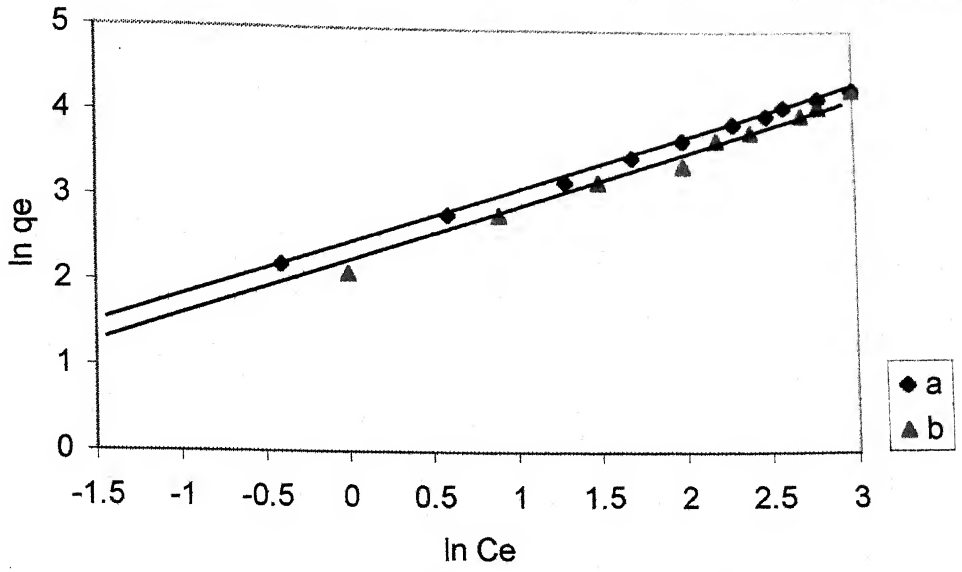


Fig 38 Freundlich adsorption isotherm of Aniline Blue a - 20°C b-30°C (Particle size- 180 Mesh)

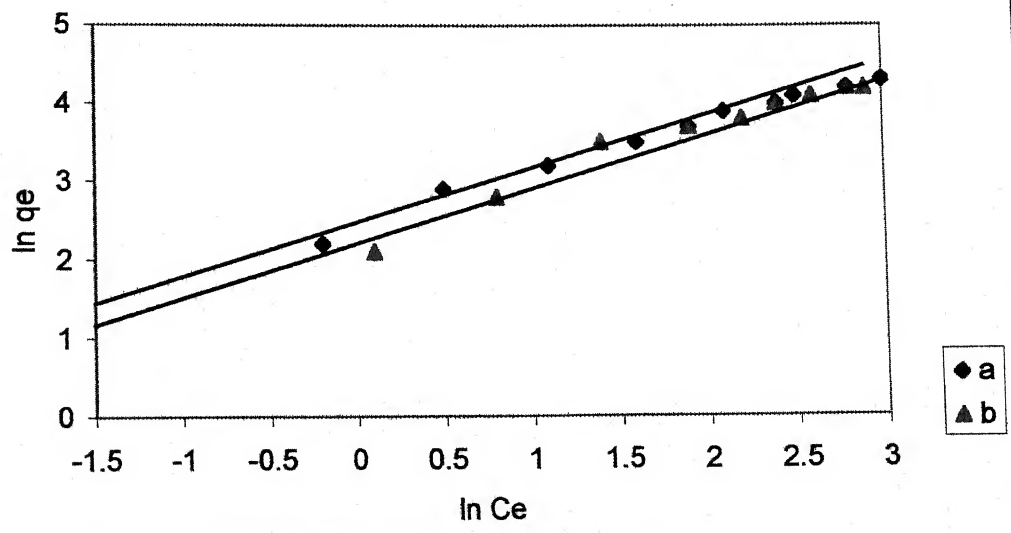


Fig 39 Freundlich adsorption isotherm of Anilene Blue a-20°C b-30°C (Particle size- 150 Mesh)

Effect of pH :- The effect of pH on adsorption of Aniline Blue dye showed in Fig 40. The percentage adsorption of Aniline Blue dye were 36.40, 44.40, 53.20, 63.60, 78.40, 82.40, 88.00, 94.00, 96.00 and 90.40 with increasing pH value from 2.5 to 11.5 at temperature 30^0C and concentration 25 mg/l. (Table 45). It was observed that with the increased of pH from 2.5 to 10.5 the adsorption of Aniline Blue dye increase from 36.40 to 96.00 % by eucalyptus wood charcoal and above the pH of 10.5 the adsorption was found to decrease gradually.

Table 45

Adsorption of Aniline Blue at different pH , Temperature 30 ^{0}C initial concentration 25 mg/l

S No	pH	Equilibrium dye concentration (mg/l)	Amount of dye adsorbed (mg/gm)	% adsorption
1	2.5	15.9	9.1	36.40
2	3.5	13.9	11.9	44.40
3	4.5	11.7	13.3	53.20
4	5.5	9.1	15.9	63.60
5	6.5	5.4	19.6	78.40
6	7.5	4.4	20.6	82.40
7	8.5	3.0	22.0	88.00
8	9.5	1.5	23.5	94.00
9	10.5	1.0	24.0	96.00
10	11.5	2.4	22.6	90.40

Table 46

Freundlich Constant for Aniline Blue

Particle Size	Temperature	K_f	1/n
180 Mesh	20^0 C	2.43	0.630
	30^0 C	2.11	0.708
150 Mesh	20^0 C	2.46	0.639
	30^0 C	2.23	0.710

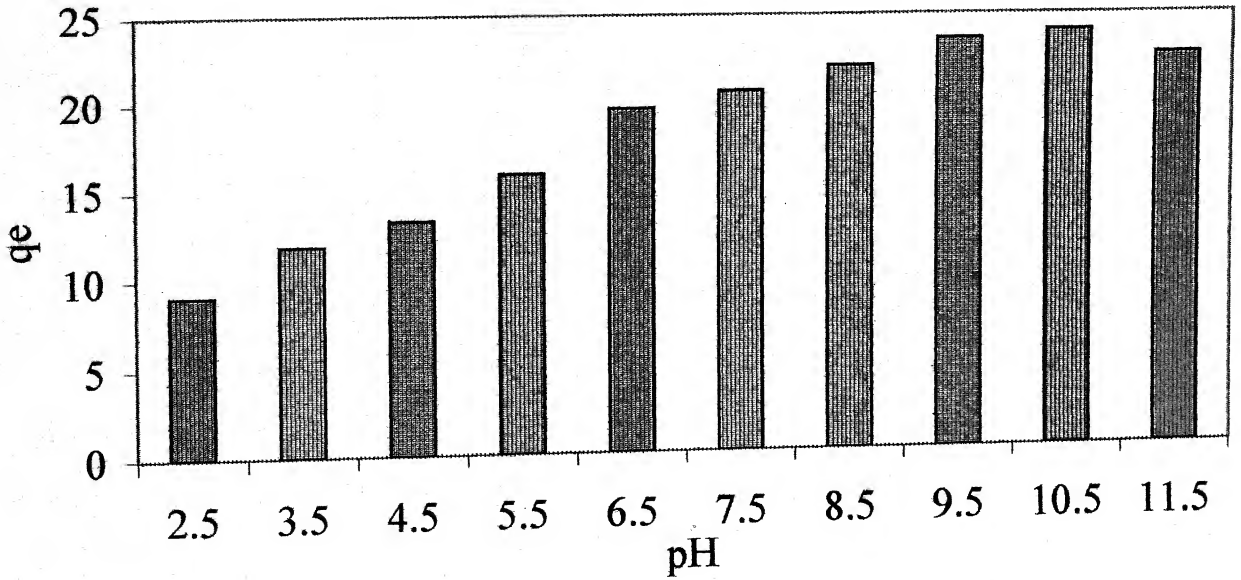


fig 40 Adsorption of Aniline Blue at different pH, Temperature 30 °C, Initial dye concentration 25 mg/l

discussion

DISCUSSION

The striking feature of good adsorption as exhibited by the eucalyptus wood charcoal is corroborated by the facts illustrated in the previous chapters by various tables and graphs. Adsorption to the extent of 90-100% has been recorded for some of the dyes. Not only this, the minimum adsorption of not less than 75% reveals the amount of potential which this adsorbent has for various dyes, may be natural or synthetic.

It was recorded that there was cent percent adsorption of Crystal Violet on eucalyptus charcoal. The charcoal as produced by the eucalyptus wood showed good adsorption for dyes e.g. Methylene Blue and Safranine, though the minimum adsorption observed was that of RhodamineB. The adsorption of the six dyes were found to be in the following decreasing order:
Crystal Violet>Methylene Blue>Safranine>Malachite Green>Aniline Blue>RhodamineB.

In this study,all basic dyes were used it was observed that, comparatively, basic dye is easily removed than acid and reactive dye. This may be due to ionic attraction between negatively charged active

centers (associated with most carbons) and positively charged basic dye molecules[273, 87].

In all the cases, it was observed that the percentage adsorption increased with increase in agitation time and attains equilibrium with-in 90 min for each concentration, this investigation has been observed by several workers[28,158]. All the straight line plots of log (qe-q) versus t at different concentration indicates that the process involves first order kinetics. This has been confirmed by earlier investigations also[24].

It was observed without exception that the removal of dye increased with the increase of initial dye concentration, but the percentage of adsorption decreased. Percent adsorption of dyes decreased with the increase of initial dye concentration, showing the process to be highly dependent on the concentration of the solution. The examination of all the plots also showed that the amount of adsorbed dye increased with increase in concentration of the dyes solutions. Several investigations supported this investigation[158,294]. All the curves were found to be smooth and continuous in nature indicating the formation of monolayer coverage of the outer surface of the adsorbent[300].

It was observed that percentage of adsorption increased with increasing dilution. This increase in adsorption with increase in dilution is explicable on the basis that more and more surface sites per gram of adsorbent are available for adsorption of adsorbate solution[23,302].

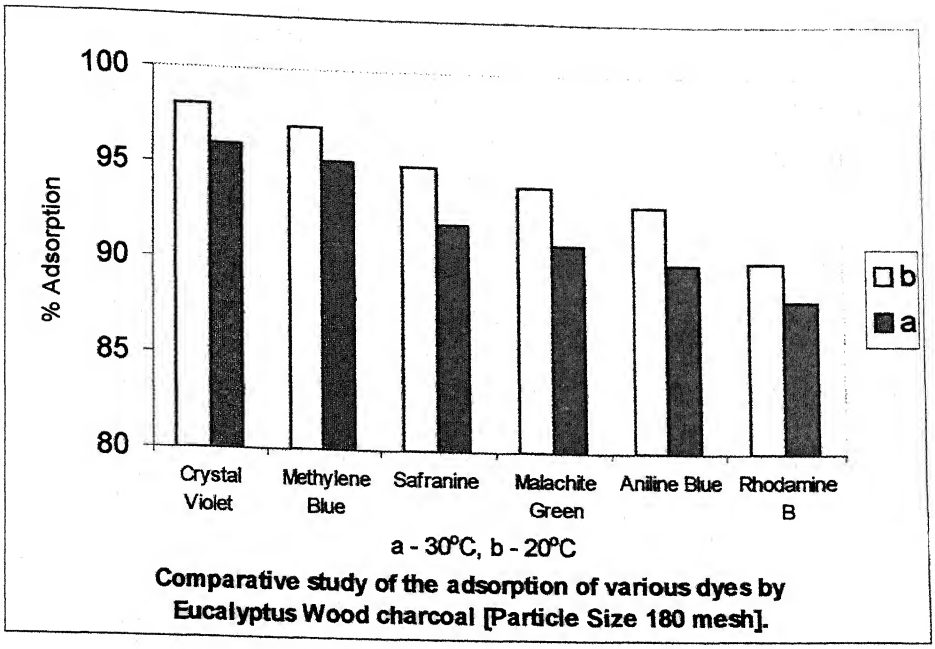
It was found in all the cases, without any contradictions, that adsorption increased with the decrease in particle size. The finer particles of eucalyptus wood charcoal of 180 mesh size exhibited more adsorption than 150 mesh particles. All the adsorbates (dyes) showed more adsorption for particles of size 180 mesh which clearly indicated significant role of particle size in adsorption process.This observation was in agreement with the earlier results[24] that as the particle diameter decreased the adsorption increased which was due to the large surface area associated with smaller particles. For larger particle size, less surface area would be available and consequently, the amount of dye adsorbed was small. For small particles, more surface area of the adsorbent would be available. McKay[176] also observed that adsorption increased with the decrease in particle size. The increase in surface area of adsorbent played an important role in boosting the retainment of adsorbate particles, which was also confirmed by the earlier

investigation[303]. According to some workers[304] the breaking of large particles tend to open tiny cracks and channels on the particle surface providing added surface area which could be employed in the adsorption process. However, insignificant increase in adsorption was reported by Dave[305]. Aggarwal and coworkers[306] investigated that there was no direct relation-ship between adsorption and surface area. It appeared that surface area was not the only factor which determined the adsorption of the adsorbate.

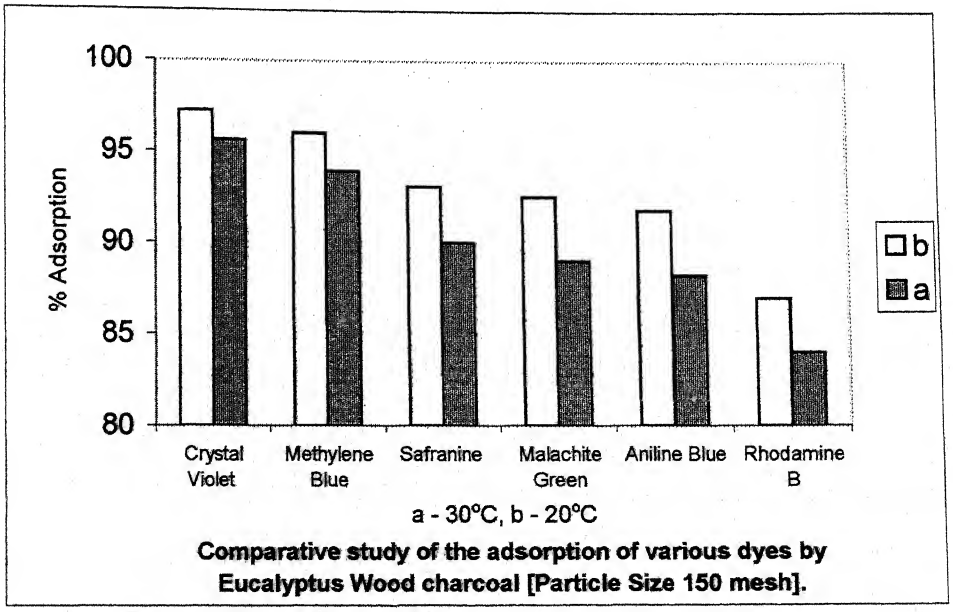
In this study, all the results indicated that the adsorption decreased with the rise of temperature. At 20^0C percent adsorption was comparatively higher than 30^0C. This tendency was confirmed by the earlier investigation[280]. This kind of decrease in adsorption with the increase of temperature was a clear indication for the exothermic nature of the process[307]. Similar type of negative temperature effects, observed for the basic dyes adsorption on natural adsorbent[308], was suggestive that the process was exothermic in nature and that the decrease in adsorption with the rise of temperature might be due to the enhanced escaping tendency of the molecules from the surface of the adsorbent. The shape of the curves obtained in present investigation was favourable for adsorption.

On the other hand, contradictory finding were noticed where adsorption of dyes at higher temperature was found to be greater compared to that at the lower temperature[222] and increase in temperature results in increased adsorption. In contradictory finding one more explanation has been placed[275] according to which, the rate of adsorption of solution increased with increasing temperature. This indicates that the adsorption process was chemi-sorption between adsorbate and adsorbent.

In all the cases the values of $-\Delta G$ were found to be negative. The negative values of $-\Delta G$ indicated the feasibility of the process and the spontaneous nature of the process and showed the high affinity of dye molecules for the adsorbent[307]. It has been noted that free energy ΔG also decreases with the rise of temperature.



Comparative study of the adsorption of various dyes by Eucalyptus Wood charcoal [Particle Size 180 mesh].



Comparative study of the adsorption of various dyes by Eucalyptus Wood charcoal [Particle Size 150 mesh].

The values of ΔH were found to be negative, which also confirmed the exothermic nature of the process and the possibility of strong bonding between adsorbate and the adsorbent[308]. The enthalpy of adsorption in all the cases was found to be in the range of -15.84 to -52.89kJ/mole indicating the process to be physical adsorption. The values of ΔS were found to be negative in all the cases and suggested that the probability of favourable adsorption and the random nature of the adsorbing molecules[308]. On the other hand, contradictory findings was noticed where the positive values of ΔH supported the endothermic nature of the process and the positive values of ΔS indicates some structural change in the adsorbate and also reflect the affinity of adsorbent for Copper (II) ions under consideration. The positive value of ΔS also indicates the increase in the randomness during the adsorption of Copper (II) on to the modified sawdust[277].

Carbon generated from agricultural products usually carries a surface charge, which is dependent on the pH of the solution. The chars of eucalyptus wood (basically constituted of lignin and cellulose) become negatively charged when its surface comes in contact with water. Basic dyes are ionised in solution to give coloured cationic dye base.

In the entire study, it has been noticed that adsorption increased with the increase of pH. Significant adsorption was observed at high pH at which adsorbent surface is negatively charged and adsorbate surface is positively charged and therefore the interaction is that of electrostatic attraction. This is attributed to the increase of electronegative charge on the adsorbent surface as the pH of the solution increases. As the adsorbent surface is negatively charged in the presence of OH^- ions the increase in electrostatic attraction between positive adsorbate (dye^{++}) and negatively charged adsorbent particles would lead to increased adsorption of dyes[308]. On the other hand contradictory finding was noticed, according to this investigation[24] the percent adsorption of dye was increased with the decrease in pH of the solution.

In view of the above, the eucalyptus wood charcoal emerged to be an excellent adsorbent both for industry and laboratory. Its importance lies in the fact that it's processing involves simple methods of grinding and activation paving a way for another economical, simply obtained, abundantly available adsorbent.

Finally, though the studies were kept limited to few dyes and few parameters there is an unlimited scope for the study of the same charcoal on various

other varying conditions and the behaviour of the same on other coloured, non-coloured, various other impurities of water and non-aqueous liquids as well as solids and gases.

conclusion

CONCLUSION

Thus, from the above studies we can establish the following:

1. The eucalyptus wood charcoal is introduced as a new adsorbent. It is cheap and is easily available. Its higher carbon content and rapid growth characteristics makes it an adsorbent, having lot of potential for use in industry.

2. The adsorption of dyes by eucalyptus wood charcoal follows first order kinetics.

3. Adsorption of dyes was highly dependent on concentration.
   (a) % adsorption α dilution.
   (b) % adsorption α 1/concentration.

4. Size of particles of adsorbent plays an important role in the adsorption process.
   % adsorption α 1/ particle size of adsorbent

5. Adsorption process was temperature dependent and found to be exothermic in nature.
   % adsorption α 1/ temperature

6. The process was found to be physical in nature involving little change in enthalpy.

7. The adsorption process obeys the Freundlich adsorption isotherm. The value of K and 1/n indicate the greater affinity for dyes by this adsorbent.

8. The maximum adsorption of dyes occurred at pH 10.5 and temperature 30°C.

9. The technique may be helpful for designing and fabricating effluent treatment plants in various industries using dyes and chemicals.

So, the use of eucalyptus wood charcoal to remove dyestuff from wastewater is a programme aiming at cleaning up the environment by the use of low cost adsorbent. It is economical on a large scale as eucalyptus wood is inexpensive and is abundantly available.

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